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16. ABSTRACT

The overall objective of the research conducted under this project was to define the chemical equilibrium between trace metals and the soluble and insoluble organic and inorganic fractions of sewage sludges and sludge-amended soil. This report is divided according to tasks carried out to fulfill this objective. The adaptation and development of a computer program, GEOCHEM, for prediction of the distribution of chemical species in soil solution is described in Section I. Research on the fractionation and characterization of sewage sludges is discussed in Section II. Studies on sludge decomposition and extractability of added metals from sludge-amended soils are discussed in Section III. Infrared studies of soluble components in water extracts of the sludge-amended soils as well as speciation data obtained from the GEOCHEM program are also reported in Section III. Research related to partitioning trace metals in sludge-amended soils into various forms by a fractionation procedure is discussed in Section IV. Considered collectively these research tasks have contributed significantly to the understanding of reactions and forms of metals in soils amended with sewage sludge.

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DETERMINATION AND PREDICTION OF CHEMICAL FORMS OF TRACE METALS IN SEWAGE SLUDGE AND SLUDGE-AMENDED SOILS

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report summarizes the results of a series of experiments designed to evaluate the chemical equilibrium between trece metals and the soluble and insoluble organic and inorganic fractions of sewage sludges and sludge-amended soil. The results make a significant contribution to the understanding of reactions and forms of metals in soils amended with sewage sludge.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

The overall objective of the research conducted under this project was to define the chemical equilibrium between trace metals and the soluble and insoluble organic and inorganic fractions of sewage sludges and sludge-amended soil. This report is divided according to tasks carried out to fulfill this objective. The adaptation and development of a computer program, GEOCHEM, for prediction of the distribution of chemical species in soil solution is described in Section 1. Research on the fractionation and characterization of sewage sludges is discussed in Section II. Studies on sludge decomposition and extractability of added metals from sludge-amended soils are discussed in Section III. Infrared studies of soluble components in water extracts of the sludge-amended soils as well as speciation data obtained from the GEOCHEM program are also reported in Section III. Research related to partitioning trace metals in sludge-amended soils into various forms by a fractionation procedure is discussed in Section IV. Considered collectively these research tasks have contributed significantly to the understanding of reactions and forms of metals in soils amended wth sewage sludge.

This report was submitted in fulfillment of Grant No. R-804516 by the Department of Soil and Environmental Science, University of California, under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from 9/76 to 12/82, and the work was completed as of 10/80.

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SECTION 1

GEOCHEM -- A COMPUTER PROGRAM FOR CALCULATING TRACE METAL EQUILIBRIA IN SOIL SOLUTIONS AFFECTED BY THE APPLICATIONS OF SEWAGE SLUDGES.

A computer program, GEOCHEM, was developed for the purpose of calculating trace metal equilibria in soil solutions affected by the application of sewage sludges. The structure of the program and a number of typical applications are described in the following subsections. Subsection 1.1 provides a discussion of the development of the program and the input data required by it in order to make a calculation. Subsection 1.2 discusses speciation calculations for saturation extracts obtained from soils, while subsections 1.3, 1.4, and 1.5 discuss the inclusion of precipitation, redox, adsorption, and exchange reactions in the calculations. Subsection 1.6 describes how soil solutions which can exchange CO_2 with the atmosphere are handled. Subsections 1.7 and 1.8 discuss special output features of the program and the method for modifying the program data bank, respectively.

1.1. INTRODUCTION TO GEOCHEM

Development of the program

GEOCHEM is a multipurpose computer program for calculating the equilibrium speciation of the chemical elements in a soil solution. The method of calculation employed in the program is based in chemical thermodynamics. For each component of a soil solution, a mole balance equation is set up and thermodynamic equilibrium constants corrected for ionic strength are incorporated into the various terms of this equation according to the law of mass action. The solution of the set of non-linear algebraic equations which results from mole balance applied to all the components simultaneously ultimately provides the concentration of each dissolved, solid, and adsorbed specie in the soil system under consideration. Some typical applications of GEOCHEM would include: (1) prediction of the concentrations of inorganic and organic complexes of a metal cation in a soil solution, (2) calculation

of the concentration of a particular chemical form of a nutrient element in a solution bathing plant roots so as to correlate that form with nutrient uptake, (3) prediction of the fate of a pollutant metal added to a soil solution of known characteristics, and (4) estimation of the effect of changing pH, ionic strength, redox potential, water content, or the concentration of some element on the solubility of a chosen chemical element in a soil solution.

GEOCHEM is a modified version of the computer program REDEQL2, which was developed at the California Institute of Technology by F.M.M. Morel, R. E. McDuff, and J. J. Morgan. The detailed structure of REDEQL2 has been described in several published articles (Morel and Morgan, 1972; Morel et al., 1973; Morel and Yeasted, 1977) and in two reports (McDuff and Morel, 1973; Ingle et al., 1978). The methods of numerical analysis employed in the program are discussed by Morel and Morgan (1972) and are compared with the methods used in other computer programs by Leggett (1977). The potential user of GEOCHEM would be well advised to study these articles and especially the two reports if he or she wishes to have more than a casual understanding of the development of the program. GEOCHEM differs from REDEQL2 principally in containing more than twice as much thermodynamic data; in utilizing thermodynamic data which have been selected critically especially for soil systems; in containing a method for describing cation exchange, and in employing a different subroutine for correcting thermodynamic equilibrium constants for the effect of nonzero ionic strength.

General features of the program

GEOCHEM is written in IBM 360 FORTRAN IV and is compatible with the G compiler, level 21.7. The program requires about 200K of core. For any soil solution data to be analyzed by the program, the chemical components are identified as metals and unprotonated ligands rather than, say, complexes and solids containing metals and ligands. The principal variables considered by the program are the free ionic concentrations of the metals and ligands. Accordingly, the mole balance equation for a metal M is written in the form:

$$M_T = [M^{n+}] + \Sigma\nu\, {}^{c}K_{\alpha\gamma\beta}\, [M^{n+}]^{\alpha}\, [H^{+}]^{\gamma}\, [L^{p-}]^{\beta} \qquad (1)$$

where M_T is the total molar concentration of the metal, ${}^{c}K_{\alpha\gamma\beta}$ is the conditional stability or formation constant for the compound $M_{\alpha}H_{\gamma}L_{\beta}$, H refers to the proton, and L refers to a ligand. The conditional stability and formation constants ${}^{c}K_{\alpha\gamma\beta}$ are discussed in subsections 1.2 and 1.3, respectively, as is the notation employed for a compound. The point to be made here is that Eq. (1) and the analogous expression for the total molar concentration of a ligand, L_T, are nonlinear algebraic equations in the free ionic concentrations. The numerical analysis problem solved by GEOCHEM is to calculate the set of free ionic concentrations that satisfies a given set of mole balance equations (one

equation for each metal and each ligand in the system being investigated), subject to input values of the M_T and L_T along with the thermodynamic equilibrium constants $K_{\alpha\gamma\beta}$ which are stored in the program. During the computation, the ionic strength is calculated using the current values of the concentrations of all charged species that are possible and the ${}^{c}K_{\alpha\gamma\beta}$ are computed in the usual way with the values of the $K_{\alpha\gamma\beta}$ and with single-ion activity coefficients (see, e.g., Stumm and Morgan, 1970). Thus the computer calculation is done self-consistently, with the total analytical concentrations and the thermodynamic equilibrium constants corrected for ionic strength related through mole balance.

GEOCHEM currently stores thermodynamic data for 36 metals and 66 ligands. These metals and ligands are listed in Table 1 along with their code numbers (also called "INMAT numbers") and code symbols. For a given metal-ligand combination, up to six soluble complexes and up to three solids can be considered by the program. In addition to the three solids per metal-ligand combination, mixed solids containing more than one metal or ligand are included in the program as indicated in Table 2. Formation constants for up to 20 mixed solids may be incorporated into GEOCHEM; at present there are 18 included.

GEOCHEM can describe soil solution equilibria in which the partial pressures of N_2, O_2, and CO_2 are permitted to vary (see subsection 1.6). The variation in O_2 pressure is treated as an oxidation-reduction phenomenon through the inclusion of 24 redox equations in the program. These redox equations are listed in Table 3. A full discussion of redox equilibria is given in subsection 1.4.

There are several specific characteristics of GEOCHEM that should be kept in mind as the description of how to use the program is read. These characteristics are most conveniently emphasized by the following list.

(1) The data bank of GEOCHEM consists of thermodynamic data at 25°C and 1 atmosphere. Therefore, all equilibrium calculations are performed at this fixed temperature and pressure. It is possible for a user to run equilibrium computations on GEOCHEM at temperatures and pressures other than 25°C and 1 atmosphere provided that a separate data bank is compiled by the user for the temperature and pressure of interest.

(2) An accounting for metastable species and species that are not favored kinetically can be incorporated into the computation by methods which are described in subsections 1.2 through 1.6. It is not necessary to assume complete thermodynamic equilibrium in order to do a calculation.

(3) The condition of electroneutrality is <u>not</u> imposed during a computation performed by GEOCHEM. The only constraint imposed is that of mole balance (i.e., mass conservation), as discussed above. The fact that charge conservation is not considered by the program has the advantage that analytical data in which, for reasons of experimental error or omission, the equivalents of metals do not equal the equivalents of ligands may still be analyzed for speciation. On the other hand, there is no guarantee that the weighted sum of positively-charged species will

TABLE 1. CODE NUMBERS AND SYMBOLS FOR THE METALS AND LIGANDS CONSIDERED BY GEOCHEM

Metals

1.	Ca^{2+}	8.	Mn^{2+}	15.	Pb^{2+}	22.	Li^{+}	29.	Ce^{3+}
2.	Mg^{2+}	9.	Cu^{2+}	16.	Co^{2+}	23.	Be^{2+}	30.	Au^{+}
3.	Sr^{2+}	10.	Ba^{2+}	17.	Co^{3+}	24.	Sc^{3+}	31.	Th^{4+}
4.	K^{+}	11.	Cd^{2+}	18.	Ag^{+}	25.	TiO^{2+}	32.	UO_2^{2+}
5.	Na^{+}	12.	Zn^{2+}	19.	Cr^{3+}	26.	Sn^{2+}	33.	Cu^{+}
6.	Fe^{3+}	13.	Ni^{2+}	20.	Al^{3+}	27.	Sn^{4+}	34.	CH_3Hg^{+}
7.	Fe^{2+}	14.	Hg^{2+}	21.	Cs^{+}	28.	La^{3+}	35.	Rb^{+}
								50.	H^{+}

Ligands*

1.	CO_3^{2-}	13.	$S_2O_3^{2-}$	25.	$GLUT^{2-}$	37.	ASP^{-}	49.	SO_3^{2-}	61.	BES^{-}
2.	SO_4^{2-}	14.	CN^{-}	26.	PIC^{-}	38.	SER^{-}	50.	SCN^{-}	62.	ClO_4^{-}
3.	Cl^{-}	15.	AC^{-}	27.	NTA^{3-}	39.	ALA^{-}	51.	NH_2OH	63.	$CBER^{-}$
4.	F^{-}	16.	$ACAC^{-}$	28.	$EDTA^{4-}$	40.	TYR^{2-}	52.	MoO_4^{2-}	64.	$CHAM^{-}$
5.	Br^{-}	17.	CIT^{3-}	29.	$DCTA^{4-}$	41.	MET^{-}	53.	WO_4^{2-}	65.	FOR^{-}
6.	I^{-}	18.	OX^{2-}	30.	$CYST^{2-}$	42.	VAL^{-}	54.	AsO_4^{3-}	66.	$FUL1^{-}$
7.	NH_3^{0}	19.	SAL^{2-}	31.	NOC^{3-}	43.	THR^{-}	55.	HVO_4^{2-}	67.	$FUL2^{-}$
8.	S^{2-}	20.	$TART^{2-}$	32.	$PHTH^{2-}$	44.	PHE^{-}	56.	SeO_3^{2-}	68.	$EDHG^{4-}$
9.	PO_4^{3-}	21.	EN^{0}	33.	ARG^{-}	45.	ISO^{-}	57.	NO_3^{-}	90.	ADS1
10.	$P_2O_7^{4-}$	22.	DIP^{0}	34.	ORN^{-}	46.	LEU^{-}	58.	$DTPA^{5-}$	91.	ADS2
11.	$P_3O_{10}^{5-}$	23.	$SUSAL^{3-}$	35.	LYS^{-}	47.	PRO^{-}	59.	SeO_4^{2-}	92.	ADS3
12.	$SiO_2(OH)_2^{2-}$	24.	GLY^{-}	36.	HIS^{-}	48.	$B(OH)_4^{-}$	60.	MAL^{2-}	93.	ADS4
										94.	ADS5
										99.	OH^{-}

(Continued)

TABLE 1 (Continued)

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* AC = acetate
ACAC = acetylacetate
CIT = citrate
OX = oxalate
SAL = salicylate
TART = tartrate
EN = ethylenediamine
DIP = dipyridyl
SUSAL = sulfosalicylate
GLY = glycine
GLUT = glutamate
PIC = picolinate
NTA = nitrilotriacetate
EDTA = ethylenediaminetetraacetate
DCTA = 1,2-diaminocyclohexane-tetracetate
CYST = cysteine
NOC = nocardamine (desferri-ferrioxamine)
PHTH = phthalate
ARG = arginine
ORN = ornithine
LYS = lysine
HIS = histidine
DTPA = diethylenetriaminepentaacetate
ASP = aspartate
SER = serine
ALA = alanine
TYR = tyrosine
MET = methionine
VAL = valine
THR = threonine
PHE = phenylalanine
ISO = isoleucine
LEU = leucine
PRO = proline
MAL = maleate
BES = benzylsulfonate
CBER = Camp Berteaau montmorillonite
CHAM = Chambers bentonite
FOR = formate
FUL1 = fulvic acid ligand
FUL2 = fulvic acid ligand
EDHG = EDDHA = ethylene dihydroxy-phenyl glycine
ADS1-ADS5 = adsorption surfaces

TABLE 2. MIXED SOLIDS CONSIDERED BY GEOCHEM

Code No.	Code Name*	Code No.	Code Name*
1	CHLORITE	10	FECACARB
2	ILLITE	11	FECOCARB
3	MICCLINE	12	FEMNCARB
4	NA-MONT	13	FECUCARB
5	PBPO4CL	14	MUSCOVIT
6	FAPATITE	15	K-MONT
7	CDZNCARB	16	CA-MONT
8	CD3ZNCARB	17	MG-MONT
9	FENICARB	18	VERM

* CHLORITE = $Mg_5Al_2Si_3O_{10}(OH)_8$

ILLITE = $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$

MICCLINE = microcline

NA-MONT = $Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

PBPO4CL = $Pb_5(PO_4)_3Cl$

FAPATITE = fluorapatite

CDZNCARB = $CdZn(CO_3)_2$

CD3ZNCARB = $Cd_3Zn(CO_3)_4$

FENICARB = $Fe_9Ni(CO_3)_{10}$

FECACARB = $Fe_9Ca(CO_3)_{10}$

FECOCARB = $Fe_9Co(CO_3)_{10}$

FEMNCARB = $Fe_4Mn(CO_3)_5$

FECUCARB = $Fe_4Cu(CO_3)_5$

MUSCOVIT = muscovite

K-MONT = $K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

CA-MONT = $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

MG-MONT = $Mg_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

VERM = Mg-vermiculite

equal the weighted sum of negatively-charged species according to the electroneutrality principle. This condition may be useful when examining the speciation results for a complete and accurate set of analytical data to see if the computer results are self-consistent. If electrical neutrality is violated, the thermodynamic data that were used may need revision or augmentation.

(4) Ionic strength corrections are made in the program through the use of single-ion or single-molecule activity coefficients. The equation employed to compute the activity coefficients (at 25 C) is:

$$\log \gamma = -\frac{AZ^2 \sqrt{I}}{1+aB\sqrt{I}} + B^oI \qquad (2)$$

where $A = 0.5116$ liter$^{\frac{1}{2}}$/mol$^{\frac{1}{2}}$, $B = 0.3292 \times 10^8$ liter$^{\frac{1}{2}}$ cm/mol$^{\frac{1}{2}}$, Z is the valence of the chemical species, and I is the true ionic strength in mol/liter. The values of the parameters a and B^o in turn depend on the value of I:

(a) If $I \leq 0.5$ mol/liter, $a = 1/B$ and $B^o = 0.3AZ^2$. Thus Eq. (2) reduces to the Davies equation.

(b) If $I > 0.5$ mol/liter, $B^o = 0.041$ liter/mol and $a = 4 \times 10^{-8}$ cm, 5×10^{-8} cm, and 6×10^{-8} cm for monovalent, bivalent, and trivalent ions, respectively. In this case, Eq. (2) becomes the Helgeson (1969) equation as modified by Truesdell and Jones (1973).

(c) For neutral species, at all values of I, $B^o = 0.1$ liter/mole (see, e.g., Helgeson, 1969). Since $Z = 0$ in this case, the first term in Eq. (2) does not contribute to the calculation of γ.

Input data required by the program

To some extent the data which must be input to GEOCHEM in order for the program to do a speci tion analysis depend on the type of problem to be considered. The general requirements are as follows.

(1) Total molar concentrations of each metal and each ligand chosen from Table 1.

(2) The pH value or the total net proton concentration in mol/liter. If the pH value is available, it should be used (see subsection 1.2).

(3) If solids are to be considered, a choice must be made as to which solid phases will be permitted to precipitate during the computation.

(4) If the soil solution is to be regarded as open with respect to CO_2, the partial pressure of this gas must be imposed.

(5) If redox equilibria are important, a choice of which redox

TABLE 3. REDOX REACTIONS AND REDOX PARAMETERS IN GEOCHEM

Reaction No.	Reaction Type	M	L	CM	CL	NE*	NH†	Redox Reaction	log K	Reaction Name
1	-10	6	7	0	0	-1	0	$Fe^{3+} + e- \rightarrow Fe^{2+}$	13.0	FE2/FE3
2	-2	8	99	1	0	2	-4	$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^+ + 2e-$	41.4	MNO2
3	-2	14	99	1	0	-2	0	$Hg^{2+} + 2e- \rightarrow Hg(liq)$	29.0	HG(LIQ)
4	3	14	99	2	0	-2	0	$2Hg^{2+} + 2e- \rightarrow Hg_2^{2+}(aq)$	31.1	HG2+2
5	-2	15	99	1	0	2	-4	$Pb^{2+} + 2H_2O \rightarrow PbO_2(s) + 4H^+ + 2e-$	-49.2	PBO2
6	-10	16	17	0	0	1	0	$Co^{2+} \rightarrow Co^{3+} + e-$	-30.9	CO2/CO3
7	3	50	1	0	1	-4	0	$CO_3^{2-} + 6H^+ + 4e- \rightarrow CH_2O(aq) + 2H_2O$	13.3	CH2O
8	10	2	8	0	0	-8	8	$SO_4^{2-} + 8H^+ + 8e- \rightarrow S^{2-} + 4H_2O$	20.2	SO4/S-2
9	10	7	57	0	0	8	-9	$NH_3(aq) + 3H_2O \rightarrow NO_3^- + 9H^+ + 8e-$	-88.1	NH3/NO3
10	1	50	99	0	0	2	-2	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e-$	-60.0	H2O2
11	-10	26	27	0	0	2	0	$Sn^{2+} \rightarrow Sn^{4+} + 2e-$	-5.1	SN2/SN4
12	-2	7	8	1	2	2	0	$Fe^{2+} + 2S^{2-} \rightarrow FeS_2(s) + 2e-$	45.3	FES2

(Continued)

TABLE 3 (Continued)

13	-2	6	99	3	0	-1	-8	$3Fe^{3+} + 4H_2O + e- \rightarrow Fe_3O_4(s) + 8H^+$	18.3	FE304
14	-3	8	99	3	0	2	-8	$3Mn^{2+} + 4H_2O \rightarrow Mn_3O_4(s) + 8H^+ + 2e-$	-61.7	MN304
15	-1	8	99	1	0	1	-3	$Mn^{2+} + 2H_2O \rightarrow MnO(OH)(s) + 3H^+ + e-$	-22.9	MnOOH
16	4	19	99	2	0	6	-14	$2Cr^{3+} + 7H_2O \rightarrow Cr_7O^{2-} + 14H^+ + 6e-$	-125.0	CR207
17	5	19	99	1	0	3	-7	$Cr^{3+} + 4H_2O \rightarrow HCrO_4^- + 7H^+ + 3e-$	-68.5	HCR04
18	6	19	99	1	0	3	-8	$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e-$	-74.9	CRO4
19	-1	50	8	0	1	2	0	$S^{2-} \rightarrow S(s) + 2e-$	16.1	1S(S)
20	3	50	8	0	4	6	0	$4S^{2-} \rightarrow S_4^{2-} + 6e-$	156.7	4SJ-2
21	4	50	8	0	5	8	0	$5S^{2-} \rightarrow S_5^{2-} + 8e-$	276.0	5S5-2
22	-10	33	9	0	0	1	0	$Cu^+ \rightarrow Cu^{2+} + e-$	-2.6	CU1/CU2
23	-1	33	99	1	0	-1	0	$Cu^+ + e- \rightarrow Cu(s)$	8.8	CU(S)
24	-1	50	57	0	1	-10	12	$2NO_3^- + 12H^+ + 10e- \rightarrow N_2(g) + 6H_2O$	210.6	N2(G)

* NE = number of electrons produced in the reaction.

† NH = number of protons consumed in the reaction.

half-reactions to allow must be made and the partial pressure of N_2 must be specified if NO_3^- is one of the ligands considered.

(6) The nature of adsorbing surfaces (ZPC and other properties) must be specified if "specific adsorption" of metals is to be considered (see subsection 1.5).

The input data deck

Listed below is a summary of the information that must appear on the card deck that is input to GEOCHEM. Each of the input data deck cards is discussed in detail in the subsection indicated parentheticaly following the card format. This summary list should be consulted, after subsections 1.2 through 1.7 have been read, as a convenient guide to preparing the input data.

Card No.	Card Columns	Type of Information Entered
(0) Format I3,5X,E14.3 (Subsection 1.9).		
	1-3	ITMAX: Enter the maximum number of iterations permitted.
	4-8	Blank
	9-22	Enter convergence criterion: $EPS = \frac{\lvert \text{Calc. Tot. Conc.} - \text{Input Tot. Conc.} \rvert}{\text{Input Tot. Conc.}}$
(1) Format 16I3. All blanks are read as zeros (Subsection 1.2).		
	1-3	Number of metals including H^+
	4-6	Number of ligands including OH^-
	7-9	Number of cases to be considered. ($\leq$ 10). A case consists of total concentrations for a group of metals and ligands and pH or TOTH for that set of concentrations. Different pCO_2, pE, and pN_2, may also be specified. One or more of the above parameters may be varied from case to case. The number of metals or ligands cannot be changed although the input concentrations may be vanishingly small.
	10-12	Solid phases to consider. -1 means no solids may precipitate even when the solution is supersaturated. 0 means no solids are imposed (assumed to be in contact with the solution) but any solid may precipitate if the solution is saturated with respect to it.

Card No.	Card Columns	Type of Information Entered
		N, where $0 < N \leq 13$, is the sum of those solids imposed and those not allowed to precipitate.
	13-15	Number of surfaces adsorbing ligands (enter "zero").
	16-18	Number of surfaces adsorbing metals.
	19-21	pH, calculated or fixed? 0 means pH is specified for each case. 1 means the program will compute pH for each case. Note: If this field is 1, TOTH data card is required.
	22-24	Redox reactions. 0 means no redox reactions considered. 1 means the program will include redox reactions. Note: If this field is 1, an electron activity card and a redox reaction card are required and a pN_2 card is required if NO_3^- is present.
	25-27	Mixed solids. 0 means no mixed solids considered. 1 means some mixed solids considered. Note: If this field is 1, a mixed solids card is required.
	28-30	Ionic strength. 0 means the user specifies the ionic strength for the computer run (same value for all cases). 1 means the program will compute the ionic strength for each case.
	31-33	Selects interaction intensity and/or capacity output routine. 0 means no output. 1 means interaction capacities computed and printed. 2 means interaction intensities computed and printed. 3 means both are printed.
	34-36	0 means output routine for case progress is used. 1 means suppressed.
	37-39	0 means output routine for complex concentrations is used. 1 means suppressed.
	40-42	0 means output routine for speciation of the ions is used. 1 means suppressed.
	43-45	0 means output routine for primary distribution of species is used. 1 means suppressed.

Card No.	Card Columns	Type of Information Entered
	46-48	0 means output routine for verification of thermodynamic data is used after each case when ionic strength is calculated. 1 means suppressed after each case.

(2) Ionic strength card. Format E7.2 (Subsection 1.2).

1-7	Fixed or guessed ionic strength in units of mol/liter.

(3) Metal cards. No. of cards = no. of metals on Card No. 1 minus one. No card required for H^+. Format I2,2X,11(1X,F5.2) (Subsection 1.2).

1-2	Code number of metal. See Table 1.
6-10	Guess of the free concentration of the metal for the first case. Use -log M for molar concentration. If 0, program assumes a value of 8 (i.e., 10^{-8} M).

The following fields are for the total concentration of the metals for up to ten cases.

12-16	First case. Use -log M for molar concentration. If the first case is 0, program assumes 1 M total concentration. If any subsequent value is 0, the value from the previous case is used.
18-22	Second case. Description for this case and the remaining cases is the same as for the first case.
24-28	Third case.
30-34	Fourth case.
36-40	Fifth case.
42-46	Sixth case.
48-52	Seventh case.
54-58	Eighth case.
60-64	Ninth case.
66-70	Tenth case.

(4) Ligand cards. No. of cards = no. of ligands on Card No. 1 minus one. No card reqired for OH^-. Format I2,2X,11(1X,F5.2) (Subsection 1.2).

1-2	Code number of ligand. See Table 1.
	Description identical to card (3) except for ligand instead of metal concentrations.

Card No.	Card Columns	Type of Information Entered

(5) pH card. Format 4X,10(1X,F5.2) (Subsection 1.2).

	Case	
6-10	1	If pH is imposed, give pH for each case.
12-16	2	If pH is calculated, give a guess of pH
18-22	3	for each case. If first case is 0,
24-28	4	program assumes a value of 8. If any
30-34	5	subsequent case is 0, the value from the
36-40	6	previous case is used.
42-46	7	
48-52	8	
54-58	9	
60-64	10	

(5A) TOTH CARD. Used only if pH calculated. Format 10E7.2 (Subsection 1.2).

	Case	
1-7	1	TOTH = net concentration of protons. A
8-14	2	value must be given for each case, as a
15-21	3	molar concentration (not -log M). A zero
22-28	4	or blank means zero value for that case.
29-35	5	
36-42	6	
43-49	7	
50-56	8	
57-63	9	
64-70	10	

(6) Partial pressure of CO_2 card. Used only if ligand 1, CO_3^{2-}, is included, Format 10F5.2 (Subsections 1.2 and 1.6).

	Case	
1-5	1	Partial pressure of CO_2, pCO_2, is given
6-10	2	as -log (pressure in atmospheres). If 0
11-15	3	for the first case, no partial pressure
16-20	4	is allowed. If any subsequent value is
21-25	5	0, value from the preceding case is used.
26-30	6	(Normal partial pressure is $10^{-3,5}$ atm.)
31-35	7	
36-40	8	
41-45	9	
46-50	10	

(7) Electron activity card. Used only if redox reactions considered. Formal 10F5.2 (Subsection 1.4).

	Case
1-5, etc.	1, etc.

Card No.	Card Columns	Type of Information Entered
		-log (electron activity), pE, must be given for each case. 0 means 0. Typical values range from -4 (reducing) to +12 (oxidizing).

(8) Partial pressure of N_2 card. Used only if redox reactions considered and if NO_3^- is included. Format 10F5.2 (Subsection 1.4).

Card Columns	Case
1-5, etc.	1, etc. -log (partial pressure of N_2), pN_2, where the pressure is in atmospheres and is given for each case. If 0 for the first case, no partial pressure is allowed. If any subsequent value is 0, value from previous case is used. (Normal partial pressure is $10^{-0.1}$ atm.)

(9) Solids card. Used only if solids are imposed and/or not allowed to precipitate. Format 39I2 (Subsection 1.3).

1-2	Code number of metal in solid A. See Table 1.
3-4	Code number of ligand in solid A. See Table 1.
5-6	1, 2, or 3 depending on whether A is the first, second or third solid listed in the Thermodynamic Data File, if this solid is imposed. If the solid is not allowed to precipitate, enter -1, -2, -3 depending on its position in the Thermodynamic Data File.
7-8	Same set of 3 parameters in six columns for up to 13 solids.
9-10	Solid B.
11-12	
13-14	
15-16	Solid C, etc.
17-18, etc.	

(10) Redox reaction card. Used only if redox reactions considered. Format 21I2 (Subsection 1.4).

1-2	First redox reaction considered. Enter reaction code number from Table 3. Up to 20 reactions, two columns/reaction.
3-4	Second redox reaction.
5-6	

Card No.	Card Columns	Type of Information Entered
(11)		Mixed solids card. Used only if mixed solids considered. May be blank. Format 20I4 (Subsection 1.3).
	1-4	Mixed solid reference number from Table 2. If the number is positive the solid is imposed. If the number is negative the solid is not allowed to precipitate. A mixed solid whose number is not given is allowed to precipitate. Up to 20 solids, 4 columns/solid.
	5-8	Second mixed solid.
	9-12	
(12), (13), (14)		Cards relating to specific adsorption reactions for metal cations. (see Subsection 1.5).

1.2. CHEMICAL SPECIATION IN SIMPLE SYSTEMS

Inorganic systems

One of the simpler applications of GEOCHEM is the calculation of the distribution of metals among several possible inorganic species in an extracted soil solution. In this case there are no solid phases involved and the computation of the equilibrium condition of the solution requires only a partitioning of each metal present into free ionic, hydrolyzed, and inorganic complex forms according to the equations of mole balance and the thermodynamic complex stability constants that are appropriate for the system.

Table 4 lists analytical data obtained by routine laboratory methods for saturation extracts of three soils, Redding (Abruptic Durixeralf), Altamont (Typic Chromoxerert), and Hanford (Typic Xerorthent). These data give the total molar concentrations of the major metal and inorganic ligand constituents of the saturation extracts. This information, along with the pH values, is quite sufficient for a speciation calculation using GEOCHEM.

TABLE 4. ANALYTICAL DATA FOR SATURATION EXTRACTS OF THREE SOILS

Soil Series	pH	Ca_T	Mg_T	K_T	Na_T	CO_{3T}*	SO_{4T}	Cl_T
		- - - - - - - - - - mol/liter x 10^3 - - - - - - - - -						
Redding	5.6	0.70	1.50	0.40	2.80	1.00	2.25	2.10
Altamont	6.9	2.50	0.80	0.60	1.00	2.00	2.50	1.00
Hanford	7.7	3.35	0.85	1.00	8.70	0.80	6.25	4.80

* $CO_{3T} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3^o]$, where [ ] refers to a molar concentration.

To set up the computation, the following cards must be punched:

a. Card No. 0. Format I3,5X,E14.8

Card columns	Type of information
1-3	ITMAX: Maximum number of iterations permitted.
4-8	Blank
9-22	EPS: Convergence Criterion: |Calculated Total Concentration - Input Total Concentration| - Input total concentration

b. Card No. 1. Format 16I3

Card columns	Type of information
1-3	Number of metals, including H^+ as a metal.
4-6	Number of ligands, including OH^- as a ligand.
7-9	Number of sets of concentration data ($\leq$ 10).
10-12	Enter "-1", meaning "no solid phases permitted".
13-15	Enter "0", meaning "no adsorption of ligands".
16-18	Enter "0", meaning "no adsorption of metals".
19-21	Enter "0", meaning "pH value is fixed".
22-24	Enter "0", meaning "no redox reactions".
25-27	Enter "0", meaning "no mixed solids".
28-30	Enter "1", meaning "ionic strength to be computed".
31-33	Enter "0", meaning "no interaction intensities or capacities to be computed".
34-36	Enter "0", meaning employ OUT 1".
37-39	Enter "0", meaning employ OUT 17".
40-42	Enter "0", meaning employ OUTMAT".

43-45	Enter "0", meaning employ OUT138".
46-48	Enter "0", meaning employ OUTCST".

Comments: Columns 28-30 instruct the program either to compute ("1") or not compute ("0") the ionic strength of the solution. OUT 1 is a subroutine that summarizes in a table the total and free ionic concentrations of the system components. OUT 17 tabulates the concentrations of the metal complexes as pC (= -log molar concentration) values. OUTMAT prints a matrix of the negative common logarithm of the sum of the concentrations of the complexes between each metal and all the ligands. OUT138 prints the mole percentage distribution of each system component among all the possible chemical forms it can have. OUTCST tabulates the thermodynamic data employed in the computation (as values of 10^2 log K) after they have been adjusted according to the value of the calculated ionic strength. Any of these output subroutines can be suppressed by entering "1" instead of "0" at the appropriate place in columns 34-48.

c. Card No. 2. Format E7.2

Enter a guess for the ionic strength, in mol/liter, for the first set of concentration data. If "0" were entered in columns 28-30 of Card No. 1, the ionic strength value entered on Card No. 2 would be that imposed as a fixed value for each equilibrium computation to be done.

d. Card No. 3A. Format I2,2X,11(1X,F%.2)

Card columns	Type of information
1-2	Enter the code number for one of the metal components as given in Table 1.
6-10	Enter a guess for the negative common logarithm of the molar free ionic concentration of the metal.
12-16	Enter the negative common logarithm of the total molar concentration of the metal (pC) for the first case.
18-22, etc.	Enter pC for the second case and continue similarly for the rest of the cases, up to 10.

e. Card No. 3B, etc.

Repeat what was entered on Card No. 3A for each metal being considered, except H^+. Do not prepare a card for H^+.

f. Card No. 4A, 4B, etc. Format I2,2X,11(1X,F5.2)

Repeat for each ligand component the kind of data that were entered on Cards 3A, 3B, etc. Do not include OH^- as one of the ligands.

g. Card No. 5. Format 4X,11(1X,F5.2)

Enter the pH values imposed for each of the sets of concentration data.

h. Card No. 6. Format 10F5.2

If CO_3 is one of the ligands in the system, the value "0" must be entered for each set of concentration data. This number is read by the program to mean "no partial pressure of CO_2 is imposed", i.e., the system is closed with respect to CO_2.

An example of the punched-card format for the saturation extract data is shown in Table 5. In Tables 6-12 the output from GEOCHEM for the Redding soil extract is given. Note that 32 soluble complexes, including hydrolytic species, were possible in the soil solution, according to the thermodynamic data stored in the program. These complexes, according to Table 9 were carbonate, sulfate, chloride, and hydroxy complexes of the metal cations, including H^+. (The row of three digits following the value of pC for each complex in Table 9 is a "stoichiometric index" that indicates the number of metal atoms, the number of ligand atoms, and the number of H^+ or OH^-, respectively, in the complex. The third digit is positive if H^+ is present and is negative is OH^- is present in the complex.)

Now let us consider Tables 6 and 12 in more detail. Tables 6 and 12 list the output from the subroutine OUTCST. Table 6 lists the equilibrium constants (as $10^2 \log^c K$, see description which follows) for various complexes, corrected for the guessed ionic strength listed on Card No. 2 (5.00E-3, see Table 5). These are the conditional constants with which the computations are initiated. In addition, ITMAX (maximum number of iterations permitted) and EPS (convergence criterion), listed on Card 1A (500 and 1.0E-4, respectively; see Table 5), are printed out for verification. Table 12 lists the equilibrium constants (as $10^2 \log^c K$) corrected to the actual ionic strength of the solution (1.0438073E-02, Table 8), i.e., when the computations converged (ended).

The following description applies to both Table 6 and 12. The first two columns give the metal and ligand code numbers as taken from Table 1. The columns listed under COMPLEXES give the values of $10^2 \log^c K$ followed by the three-digit stoichiometry indices for the complexes, where ^cK is the thermodynamic stability constant corrected to the ionic strength of the solution as calculated by the program. The stability constants ^cK describe chemical reactions of the form:

TABLE 5. THE PUNCHED-CARD FORMAT FOR THE ANALYTICAL DATA IN TABLE 4

IBM FORTRAN Coding Form

GX28-7327-6 U/M 050** Printed in U.S.A.

PROGRAM | PROGRAMMER | DATE | PUNCHING INSTRUCTIONS | GRAPHIC | PUNCH | PAGE OF | CARD ELECTRO NUMBER

STATEMENT NUMBER	CONTINUATION	FORTRAN STATEMENT	IDENTIFICATION SEQUENCE
500		1. 0E -4 CARD 0	
5	4	3 -1 0 0 0 0 1 0 0 0 0 0 CARD 1	
5.00E	-	3 CARD 2	
1		4.00 3.15 2.60 2.47 CARD 3A	
2		4.00 2.82 3.10 3.07 CARD 3B	
4		4.00 3.40 3.22 3.00 CARD 3C	
5		4.00 2.55 3.00 2.06 CARD 3D	
1		4.00 3.00 2.70 3.10 CARD 4A	
2		4.00 2.65 2.60 2.20 CARD 4B	
3		2.68 2.68 3.00 2.32 CARD 4C	
		5.60 6.90 7.70 CARD 5	
0.00		0.00 0.00 CARD 6	

*A standard card form, IBM electro 858137, is available for punching statements from this form

**Number of forms per pad may vary slightly

TABLE 6. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE SYSTEMS DESCRIBED IN TABLE 4

(EQUILIBRIUM CONSTANTS CORRECTED ACCORDING TO THE GUESSED IONIC STRENGTH)

INPUT DATA FOR VERIFICATION

MET	LIG*	SOLID†									COMPLEXES																				
1	1	0	0	0	0	0	0	0	0	0	0	293	1	1	0	1115	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
1	2	0	0	0	0	0	0	0	0	0	0	203	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	3	0	0	0	0	0	0	0	0	0	0	46	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	99	0	0	0	0	0	0	0	0	0	0	-1268	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	1	0	0	0	0	0	0	0	0	0	0	263	1	1	0	1105	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
2	2	0	0	0	0	0	0	0	0	0	0	193	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	3	0	0	0	0	0	0	0	0	0	0	36	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	99	0	0	0	0	0	0	0	0	0	0	-1188	1	0	-1	-3963	4	0	-4	0	0	0	0	0	0	0	0	0	0	0	0
4	1	0	0	0	0	0	0	0	0	0	0	76	1	1	0	1001	1	1	1	50	2	1	0	0	0	0	0	0	0	0	0
4	2	0	0	0	0	0	0	0	0	0	0	76	1	1	0	171	1	1	1	130	2	1	0	0	0	0	0	0	0	0	0
4	3	0	0	0	0	0	0	0	0	0	0	-36	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	99	0	0	0	0	0	0	0	0	0	0	-1451	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	1	0	0	0	0	0	0	0	0	0	0	46	1	1	0	1031	1	1	1	-89	2	1	0	0	0	0	0	0	0	0	0
5	2	0	0	0	0	0	0	0	0	0	0	96	1	1	0	181	1	1	1	130	2	1	0	0	0	0	0	0	0	0	0
5	3	0	0	0	0	0	0	0	0	0	0	-16	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	99	0	0	0	0	0	0	0	0	0	0	-1421	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50	1	0	0	0	0	0	0	0	0	0	0	1018	0	1	1	1653	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0
50	2	0	0	0	0	0	0	0	0	0	0	188	0	1	1	-846	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0
50	3	0	0	0	0	0	0	0	0	0	0	-844	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50	99	0	0	0	0	0	0	0	0	0	0	0	0	0	-0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

ITMAX = 500 EPS = 0.99999990E-04

†Since no solid phases were permitted to form in the computation, no data for the 7 possible solids were printed.

TABLE 7. DESCRIPTION OF THE SYSTEM AND INPUT DATA FOR THE SATURATION EXTRACTS

THESE COMPUTATIONS INVOLVE 5 METALS, 4 LIGANDS, 32 COMPLEXES AND 7 POSSIBLE SOLIDS.

IONIC STRENGTH = 0.4999999E-02

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

3 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT*	GUESS	TOTCC 1	TOTCC 2	TOTCC 3
CA	1	4.000	3.150	2.600	2.470
MG	2	4.000	2.820	3.100	3.070
K	3	4.000	3.400	3.220	3.000
NA	4	4.000	2.550	3.000	2.060

LIGAND	#INMAT*	GUESS	TOTCC 1	TOTCC 2	TOTCC 3
CO3-	1	4.000	3.000	2.700	3.100
SO4	2	4.000	2.650	2.600	2.200
CL	3	2.680	2.680	3.000	2.320
FIXED PH			5.600	6.900	7.700

* Code number for the metal or ligand, from Table 1.

TABLE 8. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE REDDING SOIL

CASE NUMBER 1

NUMBER OF ITERATIONS = 6

NUMBER OF ITERATIONS = 9

NUMBER OF ITERATIONS = 11 *

IONIC STRENGTH = 1.0438073E-02†

FIXED PH = 5.600 COMPUTED TOTH = 0.1843486E-02

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	6.0683535E-04	3.21693	7.0794765E-04	3.15000	5.5460370E-10
MG	1.3366558E-03	2.87398	1.5135657E-03	2.82000	8.8932528E-10
K	3.9391732E-04	3.40459	3.9810827E-04	3.40000	-1.9283981E-10
NA	2.7711806E-03	2.55733	2.8183921E-03	2.55000	-1.0688432E-10
CO3-	4.7274753E-09	8.32537	1.0000013E-03	3.00000	-5.5879354E-09
SO4	1.9248503E-03	2.71560	2.2387274E-03	2.65000	1.6734703E-09
CL	2.0764563E-03	2.68268	2.0893023E-03	2.68000	-1.4460963E-10

* The last "NUMBER OF ITERATIONS" is that required to obtain convergence. Previous values are those at the times the ionic strength was recalculated.

† In units of mol/liter.

TABLE 9. OUTPUT FROM THE SUBROUTINE OUT 17 FOR THE REDDING SOIL

CONCENTRATIONS OF COMPLEXES*

CA	CO3-	8.72	1	1	0	6.10	1	1	1		
CA	SO4	4.01	1	1	0						
CA	CL	5.50	1	1	0						
CA	OH	10.33	1	0	-1						
MG	CO3-	8.68	1	1	0	5.86	1	1	1		
MG	SO4	3.77	1	1	0						
MG	CL	5.26	1	1	0						
MG	OH	9.18	1	0	-1	28.69	4	0	-4		
K	CO3-	11.03	1	1	0	7.40	1	1	1	14.72	2 1 0
K	SO4	5.42	1	1	0	10.09	1	1	1	8.31	2 1 0
K	CL	6.47	1	1	0						
K	OH	12.31	1	0	-1						
NA	CO3-	10.48	1	1	0	6.25	1	1	1	14.40	2 1 0
NA	SO4	4.37	1	1	0	9.14	1	1	1	6.62	2 1 0
NA	CL	5.42	1	1	0						
NA	OH	11.17	1	0	-1						
H	CO3-	3.81	0	1	1	3.08	0	1	2		
H	SO4	6.50	0	1	1	22.44	0	1	2		
H	CL	16.73	0	1	1						

* Expressed as -log[ ], where [ ] refers to a molar concentration.

TABLE 10. OUTPUT FROM THE SUBROUTINE OUTMAT FOR THE REDDING SOIL

	FREE MET	CO3-	SO4	CL	OH
FREE LIG		8.33	2.72	2.68	8.35
CA	3.22	6.10	4.01	5.50	10.33
MG	2.87	5.86	3.77	5.26	9.18
K	3.40	7.40	5.42	6.47	12.31
NA	2.56	6.25	4.37	5.42	11.17
HYDROGEN	5.60*	3.00	6.50	16.73	*****

Free metal and free ligand concentrations are in negative logarithm of molarities.

Each entry in this table, except for those in the "FREE LIG" row and the "FREE MET" column, is a negative logarithm of the sum of the entries in a given row of Table 9, after their conversion to molar concentrations. For example, the entry for "HYDROGEN/CO3-" is 3.00 because $3.00 = -\log(10^{-3.81} + 10^{-3.08})$ according to the data in the "H CO3-" row of Table 9.

* pH value

TABLE 11. OUTPUT FROM THE SUBROUTINE OUT138 FOR THE REDDING SOIL

PRIMARY DISTRIBUTION OF METALS AND LIGANDS*

CA		
	AS A FREE METAL/	85.7 PERCENT
	BOUND WITH CO3-/	0.1 PERCENT
	BOUND WITH SO4 /	13.7 PERCENT
	BOUND WITH CL /	0.4 PERCENT
MG		
	AS A FREE METAL/	88.3 PERCENT
	BOUND WITH SO4 /	11.2 PERCENT
	BOUND WITH CL /	0.4 PERCENT
K		
	AS A FREE METAL/	98.9 PERCENT
	BOUND WITH SO4 /	1.0 PERCENT
NA		
	AS A FREE METAL/	98.3 PERCENT
	BOUND WITH SO4 /	1.5 PERCENT
	BOUND WITH CL /	0.1 PERCENT
CO3-		
	BOUND WITH MG /	0.1 PERCENT
	BOUND WITH H /	99.7 PERCENT
SO4		
	AS A FREE LIGAND/	86.0 PERCENT
	BOUND WITH CA /	4.3 PERCENT
	BOUND WITH MG /	7.6 PERCENT
	BOUND WITH K /	0.2 PERCENT
	BOUND WITH NA	1.9 PERCENT
CL		
	AS A FREE LIGAND/	99.4 PERCENT
	BOUND WITH CA /	0.2 PERCENT
	BOUND WITH MG /	0.3 PERCENT
	BOUND WITH NA /	0.2 PERCENT

* Only values grater than or equal to 0.1 mole percent are printed.

TABLE 12. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE SYSTEMS DESCRIBED IN TABLE 4

(CONSTANTS CORRECTED TO THE IONIC STRENGTH OF THE SOLUTION WHEN THE COMPUTATIONS CONVERGED)

INPUT DATA FOR VERIFICATION

MET	LIG	SOLID†									COMPLEXES																				
1	1	0	0	0	0	0	0	0	0	0	0	282	1	1	0	1104	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
1	2	0	0	0	0	0	0	0	0	0	0	192	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	3	0	0	0	0	0	0	0	0	0	0	40	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	99	0	0	0	0	0	0	0	0	0	0	-1271	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	1	0	0	0	0	0	0	0	0	0	0	252	1	1	0	1094	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
2	2	0	0	0	0	0	0	0	0	0	0	182	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	3	0	0	0	0	0	0	0	0	0	0	30	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	99	0	0	0	0	0	0	0	0	0	0	-1191	1	0	-1	-3959	4	0	-4	0	0	0	0	0	0	0	0	0	0	0	0
4	1	0	0	0	0	0	0	0	0	0	0	70	1	1	0	993	1	1	1	41	2	1	0	0	0	0	0	0	0	0	0
4	2	0	0	0	0	0	0	0	0	0	0	70	1	1	0	163	1	1	1	121	2	1	0	0	0	0	0	0	0	0	0
4	3	0	0	0	0	0	0	0	0	0	0	-38	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	99	0	0	0	0	0	0	0	0	0	0	-1451	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	1	0	0	0	0	0	0	0	0	0	0	40	1	1	0	1023	1	1	1	-96	2	1	0	0	0	0	0	0	0	0	0
5	2	0	0	0	0	0	0	0	0	0	0	90	1	1	0	173	1	1	1	121	2	1	0	0	0	0	0	0	0	0	0
5	3	0	0	0	0	0	0	0	0	0	0	-18	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	99	0	0	0	0	0	0	0	0	0	0	-1421	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50	1	0	0	0	0	0	0	0	0	0	0	1012	0	1	1	1645	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0
50	2	0	0	0	0	0	0	0	0	0	0	182	0	1	1	-852	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0
50	3	0	0	0	0	0	0	0	0	0	0	-845	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50	99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

†Since no solid phases were permitted to form in the computation, no data for the 7 possible solids were printed.

$$\alpha M + \beta L + H = M_\alpha H_\gamma L_\beta \text{ (aq)} \quad (3)$$

or

$$\alpha M + \beta L - \gamma OH + \gamma H_2O = M_\alpha OH_{-\gamma} L_\beta \text{ (aq)} \quad (4)$$

with the equilibrium constants

$$K = (M_\alpha H_\gamma L_\beta)/(M)^\alpha (H)^\gamma (L)^\beta \quad (5)$$

or

$$^*K = (M_\alpha OH_{-\gamma} L_\beta)/(M)^\alpha (OH)^{-\gamma} (L)^\beta \quad (6)$$

where M refers to the metal ion, L to the ligand, H to the proton, and OH to hydroxyl. The Greek letters are stoichiometric coefficients and ( ) refers to a thermodynamic activity. Equations (4) and (6) are employed only for hydrolytic species.

Table 7 indicates the number of chemical species, the initial guess for the ionic strength (in mol/liter), and the cases to be analyzed by the program. Table 8 applies only to the Redding soil extract (Case 1), indicating the output from the subroutine OUT 1. The true, calculated ionic strength is given along with the free ionic and total concentrations of each system component. The column headed "REMAINDER" list the values of the difference between the input total concentration of a component and the sum of the weighted concentrations of its free and complexed forms, divided by the input total concentration. This number must be less than 10^{-4} (EPS for these cases) in order for the computation to be convergent. Table 9 lists the output from the subroutine OUT 17. It may be seen that, for the Redding soil, complexes with SO_4^{2-} are the most significant ones for all the metals in the system. Table 10 gives the output from the subroutine OUTMAT, i.e., the negative logarithm of the sum of molar concentrations of, e.g., all carbonate complexes of Ca^{2+}, of Mg^{2+}, etc. Table 11 lists what is often the most useful output, the mole percentage distribution of each component among its possible chemical forms, based on the output from OUTMAT. GEOCHEM lists mole percentages only if they are at least 0.1% in value. In the case of the Redding soil, it is seen that the metals and ligands are primarily in the free ionic form, with the exception of CO_3^{2-} which is essentially all bicarbonate complex.

Organic Systems

There is no difference of principle between the calculation of chemical equilibria for inorganic systems and systems that contain organic ligands. Equations (3) to (6) apply whether L refers to

CO_3^{2-} or citrate, Cl^- or salicylate. Actually, the difference between soil solutions that contain organic compounds and those that do not is in the facts that the organic compounds in soil may be difficult to identify and characterize, that they may undergo transformations mediated biologically, and that they may form complexes of varying stoichiometry with the same metal. Once the organic compound is identified and data are available concerning its metal complexes, it may be treated just the same as, e.g., CO_3^{2-} in a calculation performed by GEOCHEM.

Table 13 lists analytical data for a saturation extract of an Altamont soil to which sewage sludge and $CdSO_4$ had been added as part of a greenhouse experiment to study Cd uptake. In this example there were 9 metals (including H^+) and 15 ligands (including OH^-) that could form 261 different complexes, according to the thermodynamic data in the program. Nine of the ligands in Table 13 are organic compounds. The concentrations of these compounds were not determined analytically, but instead were selected to provide a mixture of organic acids whose overall pH titration curve closely resembled that found experimentally for the water soluble organic fraction of sewage sludge and whose total acidity was the same as that of the sludge organics when the concentration of the latter is 10^{-3} M. The organic acids selected are representative of the types of acidic, metal-complexing functional groups in water soluble sludge organics and the concentration of 10^{-3} M is typical of what is found for organic compounds in the Altamont soil solution after the incorporation of sewage sludge. In other words, the mixture of organic acids in Table 13 constitutes a model system for the soluble, metal-complexing organic compounds in the Altamont soil during the greenhouse experiment. A detailed description of the model organic system is provided in Mattigod and Sposito (1979).

The computer cards for this example are in every way similar to what was described earlier in this section, except that now there is only one case. This case, however, requires 8 metal cards and 14 ligand cards instead of 4 metal cards and 3 ligand cards as before. The same kinds of ionic strength, pH, and carbonate cards are required as for the inorganic system.

Table 14 shows the output from the subroutine OUT138 for this example. There is much interesting information in the percentage distribution figures for the metals and ligands, but what stands out is the strong complexation of Cu(II) and Fe(III) by the organic ligands, the relative lack of complexation of Cd,Mn(II), and Zn, and the absence of metal complexes with the amino acid components. The major cations, Ca, Na, and K, appear to be involved principally with the inorganic part of the system, while Cu(II) and Fe(III) are involved principally with the organic part, with the remaining minor cations, Cd, Mn(II), and Zn, falling somewhere in between.

TABLE 13. ANALYTICAL DATA (EXPRESSED AS pC VALUES) FOR A SATURATION EXTRACT OF AN ALTAMONT SOIL AMENDED WITH SEWAGE SLUDGE AND $CdSO_4$

Component	pC*	Component	pC
Ca	2.07	CIT	4.14
K	3.70	SAL	4.27
Na	3.00	PHTH	3.97
Fe(III)	4.75	ARG	4.49
Mn(II)	4.70	ORN	4.36
Cu(II)	5.72	LYS	4.36
Cd	5.85	VAL	4.36
Zn	5.13	NO	2.17
CO_3	2.70	MAL	3.97
SO_4	2.70	BES	4.27
Cl	2.28	pH = 6.30	4.27
PO_4	4.00		

* pC = -log[ ], where [ ] refers to a molar concentration.

Code symbols for components are listed in Table 1.

TABLE 14. OUTPUT FROM THE SUBROUTINE OUT138 FOR THE SLUDGE-AFFECTED ALTAMONT SOIL

PRIMARY DISTRIBUTION OF METALS AND LIGANDS

CA		
	AS A FREE METAL /	88.6 PERCENT
	BOUND WITH CO3- /	0.6 PERCENT
	BOUND WITH SO4 /	6.9 PERCENT
	BOUND WITH CL /	1.0 PERCENT
	BOUND WITH PO4 /	0.3 PERCENT
	BOUND WITH CIT /	0.7 PERCENT
	BOUND WITH PHTH /	0.6 PERCENT
	BOUND WITH NO3 /	0.6 PERCENT
	BOUND WITH MAL /	0.6 PERCENT
K		
	AS A FREE METAL /	99.0 PERCENT
	BOUND WITH SO4 /	0.6 PERCENT
	BOUND WITH NO3 /	0.3 PERCENT
NA		
	AS A FREE METAL /	98.8 PERCENT
	BOUND WITH CO3- /	0.1 PERCENT
	BOUND WITH SO4 /	0.9 PERCENT
	BOUND WITH NO3 /	0.1 PERCENT
FE3		
	BOUND WITH CO3- /	20.6 PERCENT
	BOUND WITH CIT /	79.3 PERCENT
MN		
	AS A FREE METAL /	77.8 PERCENT
	BOUND WITH CO3- /	11.9 PERCENT
	BOUND WITH SO4 /	6.1 PERCENT
	BOUND WITH CL /	0.2 PERCENT
	BOUND WITH PO4 /	1.4 PERCENT
	BOUND WITH CIT /	0.4 PERCENT
	BOUND WITH NO3 /	1.4 PERCENT
	BOUND WITH MAL /	0.9 PERCENT
	BOUND WITH BES /	0.1 PERCENT
CO3-		
	BOUND WITH CA /	2.6 PERCENT
	BOUND WITH FE3 /	0.5 PERCENT
	BOUND WITH MN /	0.1 PERCENT
	BOUND WITH H /	96.6 PERCENT
SO4		
	AS A FREE LIGAND/	69.8 PERCENT
	BOUND WITH CA /	29.6 PERCENT
	BOUND WITH NA /	0.5 PERCENT
CL		
	AS A FREE LIGAND/	98.4 PERCENT
	BOUND WITH CA /	1.6 PERCENT
PO4		
	BOUND WITH CA /	22.3 PERCENT
	BOUND WITH NA /	0.1 PERCENT
	BOUND WITH MN /	0.3 PERCENT
	BOUND WITH H /	77.2 PERCENT
CIT		
	BOUND WITH CA /	76.9 PERCENT
	BOUND WITH FE3 /	19.5 PERCENT
	BOUND WITH CU2+ /	2.6 PERCENT
	BOUND WITH H /	0.9 PERCENT
SAL		
	BOUND WITH CA /	2.6 PERCENT
	BOUND WITH H /	97.4 PERCENT
PHTH		
	AS A FREE LIGAND/	46.4 PERCENT
	BOUND WITH CA /	49.4 PERCENT
	BOUND WITH ZN /	0.1 PERCENT
	BOUND WITH H /	4.0 PERCENT

(Continued)

TABLE 14 (Continued)

CU2+		
AS A FREE METAL /	0.3	PERCENT
BOUND WITH CO3- /	0.1	PERCENT
BOUND WITH CIT /	97.0	PERCENT
BOUND WITH ARG /	1.1	PERCENT
BOUND WITH VAL /	1.1	PERCENT
CD		
AS A FREE METAL /	62.2	PERCENT
BOUND WITH CO3- /	1.7	PERCENT
BOUND WITH SO4 /	4.9	PERCENT
BOUND WITH CL /	17.2	PERCENT
BOUND WITH PO4 /	0.5	PERCENT
BOUND WITH CIT /	4.5	PERCENT
BOUND WITH PHTH /	4.4	PERCENT
BOUND WITH VAL /	0.1	PERCENT
BOUND WITH NO3 /	1.1	PERCENT
BOUND WITH MAL /	3.4	PERCENT
ZN		
AS A FREE METAL /	69.9	PERCENT
BOUND WITH CO3- /	18.5	PERCENT
BOUND WITH SO4 /	6.9	PERCENT
BOUND WITH CL /	0.1	PERCENT
BOUND WITH PO4 /	0.7	PERCENT
BOUND WITH PHTH /	2.0	PERCENT
BOUND WITH VAL /	0.1	PERCENT
BOUND WITH MAL /	1.6	PERCENT
BOUND WITH OH /	0.1	PERCENT
ARG		
AS A FREE LIGAND/	0.1	PERCENT
BOUND WITH H /	99.8	PERCENT
ORN		
BOUND WITH H /	100.0	PERCENT
LYS		
BOUND WITH H /	100.0	PERCENT
VAL		
BOUND WITH H /	99.9	PERCENT
NO3		
AS A FREE LIGAND/	99.2	PERCENT
BOUND WITH CA /	0.8	PERCENT
MAL		
AS A FREE LIGAND/	27.5	PERCENT
BOUND WITH CA /	49.8	PERCENT
BOUND WITH MN /	0.2	PERCENT
BOUND WITH ZN /	0.1	PERCENT
BOUND WITH H /	22.4	PERCENT
BES		
AS A FREE LIGAND/	87.4	PERCENT
BOUND WITH CA /	12.6	PERCENT

Systems for which the pH value is unknown

There may be cases in which analytical data for a soil solution are available but the pH value of the solution is unknown. This situation could arise, e.g., if only the pH of a soil paste has been measured and cannot be extrapolated to get the pH of a saturation extract because of an unknown suspension effect, or if the analytical data have been obtained from a commercial laboratory where pH measurements are not routine. Another possibility is that the data to be analyzed with GEOCHEM may be composite data created for a special research purpose by adding together empirical concentration data for two solutions of very different composition (e.g., a saturation extract of a soil and an industrial wastewater). Even if the pH values of the two original solutions are available, the pH value of their mixture is not easily estimated with accuracy.

If the pH value must be computed by GEOCHEM, it is necessary to modify the computer card arrangement described earlier in this section in two ways. First, the number entered in columns 19-21 of Card No. 1 is changed to "1", meaning "pH value is to be computed", and the data entered on Card No. 5 now become gueses of the pH values for each of the sets of concentration data. These guesses play the same role as those for ionic strength in Card No. 2. The second modification is that a Card No. 5A must be inserted following Card No. 5. This new card may be described as follows:

Card No. 5A. Format 10E7.2

If pH is to be computed, enter a value for TOTH, in mol/liter, for each set of concentration data ($\leq$ 10).

The quantity TOTH is defined by the equation:

$$TOTH = \Sigma n\,[acid] + [H^+] - \Sigma m\,[base] - [OH^-] \qquad (7)$$

where [ ] refers to a molar concentration, "acid" refers to any species expected in the system that contains dissociable protons (n being the number of dissociable protons in the acid), and "base" refers to any species expected that contains dissociable hydroxyls (m being the number of dissociable hydroxyls in the base). In general, an acid is any compound with the formula H_nL, where L refers to a non-dissociable inorganic or organic ligand, as well as NH_4^+ CO_2, and SiO_2. A base is any compound with the formula $M(OH)_m$, where M refers to a metal, as well as any hydrolyzable metal oxide. Equation (7) is a statement of the "proton condition" for an aqueous solution whose components are unhydrolyzed metals and unprotonated ligands (see, e.g., Morel and Morgan, 1972; Stumm and Morgan, 1970, p. 88).

The method of calculation of TOTH can be made clear by considering some specific examples.

a. A solution containing Na_2CO_3, NaH_2PO_4, $Ca(OH)_2$, and $CaCO_3$.

$$TOTH = [NaHCO_3] + 2[NaH_2PO_4] - 2[Ca(OH)_2]$$

Note that the computation does not include Na_2CO_3 or $CaCO_3$ and that the molar concentration of NaHCO has to be estimated in some way. This could be accomplished by a good guess of the pH value and a subsequent estimate of the partitioning of CO_{3T} into $[CO_3^{2-}]$, $[HCO_3^-]$, and $[H_2CO_3]$. Even better would be a direct titrimetric determination of $[HCO_3^-]$ in the solution.

b. A solution containing dissolved CO_2 and Al_2O_3.

$$TOTH = 2[CO_2] - 6[Al_2O_3]$$

In this case the hydration of CO_2 to produce H_2CO_3 adds 2 protons per CO_2 molecule and the hydrolysis of Al_2O_3 to produce $2Al(OH)_3$ adds 6 hydroxyls per Al_2O_3 molecule.

c. A solution containing Al_2O_3, SiO_2, NH_4Cl, and CH_3CO_2H.

$$TOTH = 2[SiO_2] + [NH_4Cl] + [CH_3CO_2H] - 6[Al_2O_3]$$

Here the hydration of SiO_2 to produce H_4SiO_4 contributes 2 dissociable protons per SiO_2 molecule, $NH_4Cl = NH_3 \cdot HCl$ and acetic acid each contribute 1 dissociable proton per molecule, and the hydrolysis of Al_2O_3 contributes 6 OH^- as before.

It should be noted that TOTH need not be a positive number. In Example b, if the molar concentrations of CO_2 and Al_2O_3 happened to be the same, TOTH would equal $-4[Al_2O_3]$. For systems in which carbonate salts are present, it is best to have an experimental determination of the bicarbonate concentration if TOTH must be computed. Further discussion of TOTH is given by Ingle et al. (1978) and Morel and Morgan (1972).

1.3. SOLUBILITY EQUILIBRIA

Calculations without imposed solids

Soil solutions are always in contact with solid phases. If chemical equilibrium is assumed to exist between a soil solution and its associated solids, then important information about the solubilities of the solution components can be obtained through a calculation performed by GEOCHEM. There are three principal kinds of problems in solubility equilibria that the program can resolve:

a. Supersaturation in a metal or a ligand with respect to the most stable solid phase possible. For example, analytical data for a saturation extract taken from a calcareous soil could be checked for supersaturation in Ca with respect to $CaCO_3(s)$ in the form of calcite, or data for an acid soil could be checked for supersaturation in Al with respect to Al(OH) (s) in the form of gibbsite.

b. Precipitation or dissolution caused by the addition of a solid mixture to a soil solution. Important examples of this kind of chemical problem include the precipitation of salts or dissolution of solids induced by the application of manure, sewage sludge, or chemical fertilizer to a soil. The metal cations and the ligands (including HCO_3^- from organic matter decomposition) in an applied manure may react with the constituents of a soil solution to produce new solid phases or add to existing ones. On the other hand, the added ligands may react with metal cations already present to induce the further dissolution of an existing solid.

c. Precipitation or dissolution caused by the addition of an aqueous mixture to a soil solution. This kind of chemical problem occurs when, e.g., a soil is irrigated with water whose composition is significantly different from that of the soil solution; or a wastewater from some industrial process or agricultural operation is spilled accidentally or disposed of on land; or a geothermal brine leaks through the bottom liner of a storage lagoon and into the soil below.

Table 15 lists some analytical data pertaining to a simple situation having featurs common to both types a and b mentioned above. Except for Cd, the data are for a saturation extract of Holtville soil (Typic Torrifluvent), which is calcareous. In this case it is desired to find out if $CdSO_4$ added to the Holtville soil to produce a total concentration of 10^{-6} M Cd in the saturation extract would cause the precipitation of Cd entirely as $CdCO_3(s)$ and, if this occurred, what would be the concentraton of water-soluble Cd remaining.

The computation on GEOCHEM is set up in this case by making only a single modification in the card deck arrangement that was described in Subsection 1.2. In columns 10-12 of Card No. 1, a "0" is inserted, meaning "solids may precipitate, but none is imposed." This "0" replaces

TABLE 15. Analytical Data for a Saturation Extract of Holtville Soil

Element	pC*	Element	pC
Ca	2.28	Cd	6.00
Mg	2.64	CO_3	2.39
K	2.89	SO_4	2.12
Na	2.00	Cl	2.03

* pC = -log total molar concentration

the "-1" used previously when no solide phases were permitted. In this particular case, a "0" is retained in columns 25-27 of Card No. 1, indicating that no mixed solid is to be considered.

Table 16 shows the output from the subroutine OUTCST for the system described in Table 15. There are 51 possible soluble complexes and 10 possible solids that could form from reactions among the components, according to the thermodynamic data in the program. Under the heading "SOLID", the values of $10^2 \log {}^cK$ are given along with the stoichiometric indices for the 10 solids. The conditional equilibrium constant ${}^cK$ describes the reaction

$$\alpha M + \beta L + \gamma H = M_\alpha H_\gamma L_\beta \ (s) \qquad (8)$$

where all of the symbols have the same meaning as in Eq. (3), except that now a solid species is formed instead of a soluble complex. An equation analogous to Eq. (4) can be written for metal-hydroxy solids, also. The thermodynamic equilibrium constant for Eq. (8) is exactly analogous to K given by Eq. (5). Thus the thermodynamic K-values stored in GEOCHEM for solids are equal to the inverses of the usual solubility product constants that describe the reverse of the reaction in Eq. (8).

Table 17 shows the output from the subroutine OUT 1. It may be seen that the system described by the data in Table 15 proved to be supersaturated in Ca and Cd relative to $CaCO_3(s)$ and $CdCO_3(s)$. Of the original 5.25×10^{-3} mol/liter Ca present in the system, 2.83×10^{-3} mol/liter finally precipitated as $CaCO_3(s)$. Of the original 10^{-6} mol/

TABLE 16. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE SYSTEM DESCRIBED IN TABLE 15

(CONSTANTS CORRECTED TO THE IONIC STRENGTH OF THE SOLUTION WHEN THE COMPUTATIONS CONVERGED)

INPUT DATA FOR VERIFICATION

MET	LIG	* SOLID									* COMPLEXES																								
1	1	773	1	1	0	0	0	0	0	0	0	254	1	1	0	1078	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	2	393	1	1	0	0	0	0	0	0	0	164	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	3	0	0	0	0	0	0	0	0	0	0	22	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	99	-2315	1	0	-2	0	0	0	0	0	0	-1271	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	1	443	1	1	0	653	5	4	-2	0	0	0	224	1	1	0	1068	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	2	0	0	0	0	0	0	0	0	0	0	154	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	3	0	0	0	0	0	0	0	0	0	0	12	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	99	-1685	1	0	-2	0	0	0	0	0	0	-1191	1	0	-1	-3945	4	0	-4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	1	0	0	0	0	0	0	0	0	0	0	52	1	1	0	971	1	1	1	17	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0
4	2	0	0	0	0	0	0	0	0	0	0	52	1	1	0	141	1	1	1	97	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0
4	3	0	0	0	0	0	0	0	0	0	0	-35	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	99	0	0	0	0	0	0	0	0	0	0	-1447	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	1	77	2	1	0	0	0	0	0	0	0	22	1	1	0	1001	1	1	1	-106	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0
5	2	0	0	0	0	0	0	0	0	0	0	72	1	1	0	151	1	1	1	97	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0
5	3	0	0	0	0	0	0	0	0	0	0	-15	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	99	0	0	0	0	0	0	0	0	0	0	-1417	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
11	1	1133	1	1	0	0	0	0	0	0	0	304	1	1	0	513	1	2	0	603	1	3	0	1138	1	1	1	0	0	0	0	0	0	0	0
11	2	0	0	0	0	0	0	0	0	0	0	164	1	1	0	223	1	2	0	176	1	3	0	228	1	1	1	0	0	0	0	0	0	0	0
11	3	0	0	0	0	0	0	0	0	0	0	162	1	1	0	217	1	2	0	157	1	3	0	342	1	4	0	-877	1	1	-1	0	0	0	0
11	99	-1385	1	0	-2	0	0	0	0	0	0	-1021	1	0	-1	-2055	1	0	-2	-3335	1	0	-3	-4715	1	0	-4	-918	2	0	-1	-3265	4	0	-4
50	1	1775	0	1	2	0	0	0	0	0	0	996	0	1	1	1625	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50	2	0	0	0	0	0	0	0	0	0	0	166	0	1	1	-858	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50	3	0	0	0	0	0	0	0	0	0	0	-845	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
50	99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

TABLE 17. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE SYSTEM DESCRIBED IN TABLE 15

NUMBER OF ITERATIONS = 75

SOLID CD CO3- 1 PRECIPITATES

NUMBER OF ITERATIONS = 76

NUMBER OF ITERATIONS = 79

NUMBER OF ITERATIONS = 81

IONIC STRENGTH = 3.0750133E-02

FIXED PH = 7.900 COMPUTED TOTH = 0.1247194E-02

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	1.8540472E-03	2.73188	5.2480847E-03	2.28000	-1.0710210E-08
MG	1.8487140E-03	2.73313	2.2908757E-03	2.64000	4.9348046E-09
K	1.2608315E-03	2.89934	1.2882538E-03	2.89000	4.2022830E-11
NA	9.6562132E-03	2.01519	1.0000009E-02	2.00000	-5.1958438E-11
CD	4.6571682E-07	6.33188	1.0000031E-06	6.00000	0.0
CO3-	1.0043404E-05	4.99812	4.0738136E-03	2.39000	5.3432814E-12
SO4	6.3173249E-03	2.19947	7.5857900E-03	2.12000	7.2656832E-09
CL	9.2811882E-03	2.03240	9.3325600E-03	2.03000	-2.0891839E-09

SOLID	MOLES PER LITER OF SOLUTION
CA CO3- 1	2.8335829E-03
CD CO3- 1	1.9441893E-07

liter Cd, 1.94×10^{-7} mol/liter precipitated as $CdCO_3(s)$. The precipitation of $CaCO_3(s)$ would not be expected in a saturation extract at equilibrium. It is possible that this precipitation occurs in the calculation by GEOCHEM because the value of CO_{3T} was determined on a sample of extracted solution immediately after its withdrawal and, therefore, that the value of CO_{3T} represents an equilibrium with a partial pressure of CO_2 that is relatively high. Since the calculation by GEOCHEM treated the system as closed with respect to CO_2, $CaCO_3(s)$ was "forced" to precipitate. More will be said about this point in Subsection 1.6. Another possibility is that the data in Table 15 do not represent true equilibrium and the system is kinetically supersaturated with respect to $CaCO_3(s)$. A third possibility, of course, is that there is an experimental error in the analytical data.

Table 18 lists the output from the subroutine OUT 138. The noteworthy point here is that, when solids are involved, OUT 138 prints the mole percentage distribution of both soluble and solid species for each metal and ligand. In order to know the percentage distribution of a component among soluble species alone, it would be necessary to divide each percent figure given for the free ionic and complexed forms by the difference between 1.00 and the percent in solid form/100. Insofar as the objective in analyzing the data in Table 15 is concerned, it is seen that, under the conditions of the calculation, 19.4% of the added Cd is predicted to precipitate as $CdCO_3(s)$.

The example discussed here is a simple prototype for any calculation by GEOCHEM relating to solubility equilibria in a soil solution, provided that no solid is assumed *a priori* to precipitate and no mixed solids are involved. If mixed solids must be included in the calculation, then two things must be done. First, of course, a "1" must be entered in columns 25-27 of Card No. 1, meaning "mixed solids are considered". Secondly, a new card must be inserted after Card No. 6 (the CO_2 partial pressure card):

Card No. 11. Format 20I4

This card is left entirely blank if all of the mixed solids being considered are simply allowed to precipitate. If some of the mixed solids considered are to be prevented from precipitating, then the following card format is employed.

Card Columns	Type of Information
1-4	Enter a minus sign, then the code number of a mixed solid that is not allowed to precipitate, taken from Table 3.
5-8, etc.	Repeat the procedure for a second mixed solid that must not precipitate, etc., up to 20.

TABLE 18. OUTPUT FROM THE SUBROUTINE OUT138 FOR THE SYSTEM DESCRIBED IN TABLE 15

```
PRIMARY DISTRIBUTION OF METALS AND LIGANDS*
CA
    AS A FREE METAL/   35.3 PERCENT
    BOUND WITH CO3-/    0.4 PERCENT
    IN SOLID FORM WITH CO3-/ 54.0 PERCENT
    BOUND WITH SO4 /    9.7 PERCENT
    BOUND WITH CL  /    0.5 PERCENT
MG
    AS A FREE METAL/   80.7 PERCENT
    BOUND WITH CO3-/    0.6 PERCENT
    BOUND WITH SO4 /   17.7 PERCENT
    BOUND WITH CL  /    1.0 PERCENT
K
    AS A FREE METAL/   97.9 PERCENT
    BOUND WITH SO4 /    2.1 PERCENT
NA
    AS A FREE METAL/   96.6 PERCENT
    BOUND WITH CO3-/    0.1 PERCENT
    BOUND WITH SO4 /    3.3 PERCENT
CD
    AS A FREE METAL/   46.6 PERCENT
    BOUND WITH CO3-/    1.9 PERCENT
    IN SOLID FORM WITH CO3-/ 19.4 PERCENT
    BOUND WITH SO4 /   13.2 PERCENT
    BOUND WITH CL  /   18.7 PERCENT
    BOUND WITH OH  /    0.2 PERCENT
CO3-
    AS A FREE LIGAND/   0.2 PERCENT
    BOUND WITH CA  /    0.5 PERCENT
    IN SOLID FORM WITH CA  / 69.6 PERCENT
    BOUND WITH MG  /    0.4 PERCENT
    BOUND WITH NA  /    0.3 PERCENT
    BOUND WITH H   /   29.0 PERCENT
SO4
    AS A FREE LIGAND/  83.3 PERCENT
    BOUND WITH CA  /    6.7 PERCENT
    BOUND WITH MG  /    5.3 PERCENT
    BOUND WITH K   /    0.3 PERCENT
    BOUND WITH NA       4.3 PERCENT
CL
    AS A FREE LIGAND/  99.4 PERCENT
    BOUND WITH CA  /    0.3 PERCENT
    BOUND WITH MG  /    0.2 PERCENT
```

* NOTE: "BOUND WITH" means in complexed form and does not include solids.

For each mixed solid (up to 20) that must not precipitate, there must be an entry in Card No. 11. For each mixed solid that is allowed (but not imposed) there is no entry on the card. Regardless of whether Card No. 11 is blank or filled in, it must always be the last card in the input data deck, unless adsorption phenomena are also being considered.

When mixed solids are considered, their $10^2 \log^2 K$ values are printed as part of the output from OUTCST and they are treated the same as any other solid in the remainder of the output.

Calculations with imposed and/or unallowed solids

There are two important reasons for imposing and/or not allowing solids during a solubility equilibrium calculation performed by GEOCHEM:

a. If the system is known empirically to be supersaturated with respect to certain solid phases, then these solids can be "clamped" selectively during the calculation. The remaining solids that are possible may be allowed to precipitate or even be imposed.

b. If the solution under consideration is known empirically to be in equilibrium with one or more solid phases, or if one or more solids is expected with certainty to precipitate from the solution, these solids may be imposed on the calculation from the outset.

The possibility of not allowing certain solids in a calculation endows GEOCHEM with the flexibility to describe accurately systems that are not strictly in equilibrium with respect to solid phases. This situation could occur frequently in soil solutions.

If a solid is imposed for a calculation and actually does precipitate, according to the criteria for chemical equilibrium, a great deal of time may be saved in a computation for a large system. On the other hand, if the solid is imposed incorrectly, the computation will converge very slowly and may even be interrupted without convergence (see Subsection 1.9). In general, a solid should be expected with a high degree of certainty before it is imposed.

Before a set of solids is imposed, it should be checked for conformity with the Gibbs phase rule. If too many solids are imposed, an error message will be generated (see Subsection 1.9). The Gibbs phase rule states that the number of intensive variables* which can be varied independently in a chemical system, f, is given by the expression:

$$f = C + 2 - P \qquad (9)$$

---

* The intensive variables are temperature, pressure, and a chemical potential for each component in each phase.

where C is the number of components in the system and P is the number of phases. Since temperature and pressure are stipulated during a calculation by GEOCHEM, and since there is always an aqueous phase present, Eq. (9) may be reduced to

$$f_e = C - P_s \tag{10}$$

where P_s is the number of solid phases present and $f_e = f - 2 + P - P_s = f - 1$. The smallest value allowed for f_e is 1, because the smallest value for f is 2 if the temperature and pressure of the system always are to be stipulated at will. Now, a component is defined as a constituent whose mass can be varied independently in a closed chemical system. Therefore, in applying Eq. (10), C must be calculated by subtracting from the number of neutral compounds in the system the number of chemical reactions that are possible between those compounds (see, e.g., Guggenheim, 1967, pp. 33-34 and 265-267).

As an example, consider a closed system containing $CaCO_3$, $Ca(OH)_2$, H_2CO_3, and H_2O. Of these constituents, only three may be taken as components because of the chemical reaction

$$CaCO_3(aq) + 2H_2O = Ca(OH)_2(aq) + H_2CO_3(aq) \tag{11}$$

The maximum number of solid phases that can form in the system is, accordingly, the solution of the Eq. (10) for $f_e = 1$, i.e., $1 = 3 - P_s(max)$, or $P_s(max) = 2$ solid phases. Thus, both $CaCO_3(s)$ and $Ca(OH)_2(s)$ could be imposed for this system with no violation of the Gibbs phase rule. On the other hand, in a system containing $CaCO_3$, $MgCO_3$, $Ca(OH)_2$, $Mg(OH)_2$, H_2CO_3, and H_2O, the five solids $CaCO_3(s)$, $MgCO_3(s)$, $CaMg(CO_3)_2(s)$, $Ca(OH)_2(s)$, and $Mg_4(OH)_2(CO_3)_3(s)$ cannot all be imposed because there are four components in this system and $P_s(max) = 3$ according to Eq. (10) with $f_e = 1$.

In order to perform a calculation with GEOCHEM in which some solid phases are imposed and some are not allowed, three modifications must be made in the card deck arrangement that was described in section 2.1. First, in columns 10-12 of Card No. 1 the total number of solids imposed plus those not allowed to precipitate must be inserted. This number can be as large as 13. Also, in columns 25-27 of the same card, either a "0" or a "1" must be entered depending on whether mixed solids are to be considered, as discussed in section 3.1. Secondly, a new card must be inserted after Card No. 6:

Card No. 9. Format 39I2

Card Columns	Type of Information
1-2	Code number of the metal in a chosen solid (Table 1)
3-4	Code number of the ligand in a chosen solid (Table 1)

5-6	Enter "-1", "-2", or "-3" if the solid is not allowed, or "+1", "+2", or "+3", if the solid is imposed.according to the solid's number in the thermodynamic data file.
7-8, etc.	Repeat the procedure for each imposed or unallowed solid, up to 13.

A negative entry disallows the solid for all cases in the computation; a positive number imposes it for the first case only. The last modification to be made is the addition of the mixed solids card:

Card No. 11. Format 20I4

Card Columns	Type of Information
1-4	Enter the code number of a chosen mixed solid (Table 2) as a negative number, if the solid is not allowed, or as a positive number, if the solid is imposed.
5-8, etc.	Repeat the procedure for all imposed or unallowed mixed solids, up to 20.

Thermodynamic data for unallowed solids will not appear in the output from OUTCST. A listing of the imposed solids will be given as part of the output from OUT 1.

1.4. REDOX EQUILIBRIA

There are two different ways in which the reactions of oxidized and reduced species in a soil solution can be described with the help of GEOCHEM:

a. If there is experimental evidence that two species coupled by a redox equation occur simultaneously in significant concentrations in a soil solution, then both species should be included in the calculation as input metals or ligands and no redox equation should be considered. For example, if both $NH_3(aq)$ (i.e., NH_4^+) and NO_3^- are expected in a system, then ligands 7 and 57 in Table 1 should be included in the calculation which then proceeds as described in subsections 2 and 3. Similarly, if Fe^{3+} (SO_4^{2-}) is expected to represent virtually all of the free iron (sulfur) ions in a system, or if Fe^{2+} (S^{2-}) is expected to do the same, then one or the other of these metal (ligand) ions should be an input metal (ligand) in the calculation and the redox half-reaction between them should be ignored. In general, if experimental data indicate that redox equilibrium does not exist because of kinetic or biological

factors, or that one member of a redox couple is completely dominant, redox equations should not be included as part of the calculation by GEOCHEM. Attempts to compute the concentration of a redox species which may be present in negligible concentrations at the pE value considered may lead to nonconvergence and system generated error messages.

b. If there is reason to believe that a redox half-reaction is actually occurring in a system (e.g., SO_4^{2-} reduction to S^{2-} in a waterlogged soil), then the reaction may be included as a part of the criteria for chemical equilibrium in a calculation performed by GEOCHEM.

In order to consider redox equilibria in a computation for a soil solution, several things must be done. First, a "1" must be entered in columns 22-24 of Card No. 1, meaning "redox reactions are considered". In addition, if the redox reactions bring in metals or ligands listed in Table 1 that are not already being specified as representing a total concentration value in the analytical data for the system, these metals or ligands must be included in the data entered into columns 1-3 and 4-6 of Card No. 1. Cards similar to Card No. 3A or 4A also must be included, with the total concentration for each case set equal to 10^{-8} M so as not to alter significantly the input analytical data. For example, if the sulfur content of a soil solution is to be specified by the input total concentration of SO_4^{2-} and if redox reaction 8 in Table 3 is to be considered, then both SO_4^{2-} and S^{2-} must be accounted for in columns 4-6 of Card No. 1 and a ligand card for S^{2-} must be employed with each entry set equal to 8.0. For a given redox couple, the choice of which species to assign the total analytical concentration is, of course, arbitrary, as is the choice of which specie is to be the reactant and which the product in the half-reaction. Regardless of which specie is assigned the total analytical concentration in the input data deck, GEOCHEM assigns the total concentration always to the specie designated as the reactant in each redox half-reaction shown in Table 3. In the case of the SO_4^{2-}/S^{2-} couple, this is SO_4^{2-}; in the case of Fe^{3+}/Fe^{3+} it is also the oxidized specie. However, for the Cu^{2+}/Cu^{+} couple the reduced species has been chosen, as it has also in the case of NH_3/NO_3^-. The method of assignment of total concentrations by GEOCHEM in the case of redox couples will be made clear in the examples to be discussed later in this section.

Next, an electron activity card must be included:

Card No. 7. Format 10F5.2

Card Columns	Type of Information
1-5	Enter the value of pE = -log (electron activity) for the first case.
6-10, etc.	Repeat the procedure for each case considered.

The concept of pE has been discussed at length by Stumm and Morgan (1970, Chap. 7). The pE value plays a role in redox equilibria that is similar

to the role played by the pH value in acid-base equilibria. The relation between pE and E_H, the redox potential, is given in the expression:

$$pE = \frac{E_H}{59.155} \qquad (12)$$

where E_H is measured in millivolts. If the value of E_H is known or can be estimated for a given soil solution, the pE value is calculated according to Eq. (12). For neutral soils pE can range from about -7.0 to +14. For acidic soils, both limits shift upward by about 3 pE units while for alkaline soils they shift downward by about the same amount.

If redox reactions are being considered and NO_3^- is one of the input ligands, then a N_2 partial pressure card must be added:

Card No. 8. Format F5.2

Card Columns	Type of Information
1-5	Enter "0" if the system is closed with respect to $N_2(g)$. (Enter -log P_{N_2} otherwise.)

In this section it will be assumed that the system is closed and, therefore, that Card No. 8 contains only a "0" in columns 1-5.

Finally, a redox reaction card must be included:

Card No. 10. Format 20I2

Card Columns	Type of Information
1-2	Enter the redox reaction number from Table 3.
3-4, etc.	Repeat the procedure for a second reaction, up to 20.

With the addition of Card Nos. 7 and 10 (as well as 8 when necessary), the computation is run similarly to what was discussed in subsections 2 and 3. For purposes of calculation, redox reactions are classified into three categories in GEOCHEM. Type A reactions are those in which a complex is involved (e.g., Reaction No. 10 in Table 3). Type B reactions include a solid phase (e.g., No. 2 in Table 3), while Type C reactions relate only metals or ligands (e.g., Nos. 1 and 8 in Table 3). A given redox reaction is characterized by the parameters KRED, MREDOX, LREDOX, NELEC, NHRED, and REDCST. The values of these parameters depend on both the type and the number of the redox reaction, as indicated in Table 19. Numerical information concerning the parameters is printed as part of the output from the subroutine OUTCST.

Table 20 lists some analytical data for a saturation extract of an Altamont soil (Typic Chromoxerert) that has been amended with sewage

TABLE 19. PARAMETERS CHARACTERIZING A REDOX HALF-REACTION IN GEOCHEM

Reaction Type	KRED	MRED	LRED
A	Complex No.*	Metal No.‡	Ligand No.#
B	Minus Solid No.†	Metal No.	Ligand No.
C	-10 if 2 metals	Metal No.	Metal No.**
C	+ 10 if 2 ligands	Ligand No.§	Ligand No.

NELEC = stoichiometric coefficient of e^- in the redox reation in Table 3

NHRED = stoichiometric coefficient of H^+ in the redox reaction in Table 3

REDCST = $10^2 \log^c K$ (log K from Table 3)

*The number assigned to the complex in the thermodynamic data file (see Subsection 1.8).

†Minus the number assigned to the solid in the thermodynamic data file (see Subsection 1.8).

‡Numerical position of the reactant metal in the input list of metals.

§Numerical position of the reactant ligand in the input list of ligands.

#Numerical position of the product ligand in the input list of ligands.

**Numerical position of the product metal in the input list of metals.

TABLE 20. ANALYTIC DATA FOR A SATURATION EXTRACT OF ALTAMONT SOIL.

Component	pC	Component	pC
Ca	2.07	CIT	4.14
K	3.70	SAL	4.27
Na	3.00	PHTH	3.97
Fe	4.75	ARG	4.49
Mn	4.70	ORN	4.36
Cu	5.72	LYS	4.36
Cd	5.85	VAL	4.36
Zn	5.13	NO_3	2.17
CO_3	2.70	MAL	3.97
SO_4	2.70	BES	4.27
Cl	2.28	pH = 6.30	
PO_4	4.00		

sludge. Two examples of redox calculations involving these data will be given. In the first example, the objective is to discover whether significant concentrations of Fe(II) AND Cu(I) would exist in the Altamont soil solution when the redox potential is about +650 mV. Table 21 shows a portion of the output from the subroutine OUTCST and the complete output from the system description provided by GEOCHEM. The output from OUTCST gives the values of the six redox parameters for reactions 1 and 22 in Table 3. It may be noted that MREDOX and LREDOX are equal to 4 and 5, respectively, because Fe^{3+} and Fe^{2+} occupy the fourth and fifth positions in the list of input metals provided in the system description. For the same reason Cu^{+} and Cu^{2+} correspond to MREDOX = 10 and LREDOX = 7. NELEC is equal to -1 for reaction 1 and +1 for reaction 22 in Table 3 because of the way those reactions are written in the table. REDCST is equal to $10^2 \log^c K$, with log K as given in Table 3. Table 22 shows the output from the subroutine OUT 1. Note that the initial total concentration of Cu^{2+} is listed as 0.0 even though Table 21 shows that it was entered as $10^{-5.72}$

TABLE 21. OUTPUT FROM OUTCST FOR REDOX DATA AND DESCRIPTION OF A SYSTEM BASED ON THE ANALYTICAL DATA IN TABLE 20. (CONSTANTS CORRECTED FOR IONIC STRENGTH AT CONVERGENCE)

50	57	0	0	0	0	0	0	0	0	0	0	0	0	-148	0	1	1	0	0	0	0
50	60	0	0	0	0	0	0	0	0	0	0	0	0	596	0	1	1	776	0	1	2
50	61	0	0	0	0	0	0	0	0	0	0	0	0	59	0	1	1	0	0	0	0
50	99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

REDOX DATA	KRED	MREDOX	LREDOX	NELEC	NHRED	REDCST
	-10	4	5	-1	0	1266
	-10	10	7	1	0	-239

THESE COMPUTATIONS INVOLVE 11 METALS, 15 LIGANDS, 294 COMPLEXES AND 28 POSSIBLE SOLIDS.

IONIC STRENGTH = 0.4999999E-02

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	LIGAND	#INMAT	GUESS	TOTCC 1
CA	1	4.000	2.070	CO3-	1	2.700	2.700
K	4	5.000	3.700	SO4	2	4.000	2.700
NA	5	4.500	3.000	CL	3	4.000	2.280
FE3	6	6.000	4.750	PO4	9	5.000	4.000
FE2	7	8.000	8.000	CIT	17	5.000	4.140
MN	8	6.000	4.700	SAL	19	5.000	4.270
CU2+	9	7.000	5.720	PHTH	32	5.000	3.970
CD	11	6.000	5.850	ARG	33	5.000	4.490
ZN	12	6.500	5.130	ORN	34	5.000	4.360
CU1+	33	8.000	8.000	LYS+	35	5.000	4.360
				VAL	42	5.000	4.360
				NO3	57	3.500	2.170
				MAL	60	5.000	3.970
				BES	61	6.000	4.270

FIXED PH 6.300

REDOX POTENTIAL 11.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

FE2/FE3
CU1/CU2

TABLE 22. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE SYSTEM DESCRIBED IN TABLE 21

CASE NUMBER 1

NUMBER OF ITERATIONS = 35

NUMBER OF ITERATIONS = 39

NUMBER OF ITERATIONS = 41

IONIC STRENGTH = 2.5065232E-02

FIXED PH = 6.300 COMPUTED TOTH = 0.3510528E-02

PE = 11.00

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	7.4936673E-03	2.12531	8.5114017E-03	2.07000	4.7293238E-08
K	1.9722481E-04	3.70504	1.9952665E-04	3.70000	-6.2012340E-12
NA	9.8530855E-04	3.00643	1.0000013E-03	3.00000	-1.5822928E-10
FE3	1.2622536E-15	14.89886	1.7792830E-05	4.74975	-9.5781694E-10
FE2	5.7695222E-14	13.23886	0.0	*******	-9.5781694E-10
MN	1.7083759E-05	4.76742	1.9952669E-05	4.70000	1.8985349E-10
CU2+	6.2693495E-09	8.20278	0.0	*******	1.4824764E-10
CD	9.0309078E-07	6.04427	1.4125435E-06	5.85000	4.9427532E-11
ZN	4.9611926E-06	5.30441	7.4131376E-06	5.13000	4.0435788E-10
CU1+	1.5389755E-17	16.81277	1.9154695E-06	5.71772	1.4824764E-10
CO3-	1.6787618E-07	6.77501	1.9952657E-03	2.70000	1.2340024E-08
SO4	1.3951729E-03	2.85537	1.9952657E-03	2.70000	2.5260210E-08
CL	5.1634870E-03	2.28706	5.2480847E-03	2.28000	-1.1897628E-09
PO4	3.0834099E-11	10.51097	1.0000018E-04	4.00000	4.7903086E-09
CIT	2.8663648E-17	16.54266	7.2443858E-05	4.14000	4.8418336E-09
SAL	1.8150490E-12	11.74111	5.3703363E-05	4.27000	7.3896445E-11
PHTH	4.9751121E-05	4.30320	1.0715231E-04	3.97000	3.7772487E-09
ARG	4.1592465E-08	7.38099	3.2359472E-05	4.49000	6.6774586E-11
ORN	5.3540028E-12	11.27132	4.3651729E-05	4.36000	-1.1260681E-10
LYS	2.6873365E-12	11.57068	4.3651729E-05	4.36000	-2.6060065E-10
VAL	2.2356282E-08	7.65060	4.3651729E-05	4.36000	-7.4152240E-11
NO3	6.6271834E-03	2.17867	6.7608543E-03	2.17000	-2.4118652E-09
MAL	5.3814671E-05	4.26910	1.0715231E-04	3.97000	1.6364368E-09
BES	4.9778537E-05	4.30296	5.3703363E-05	4.27000	2.0190100E-12

M. Because Cu^+ is the reactant specie in reaction 22 it is assigned the total input concentration of Cu by GEOCHEM. The objective in doing this example is met in Table 23, which shows part of the output from the subroutine OUTMAT. It may be seen that both Fe(II) and Cu(I) are insignificant in the system at pE = 11.

As a second example, the effect of lowering the redox potential to about -120 mV on the trace metals Cd, Cu, and Zn, in regard to sulfide precipitation, may be considered. Table 24 shows part of the output from OUTCST along with the system description for this problem. Table 25 gives the output from OUT 1, which shows that essentially all of the Cd, Cu, and Zn present would precipitate as sulfides if the pE were to drop to -2. (It also turns out that the solution is supersaturated with respect to apatite.) In a more realistic simulation, redox reactions involving Cu, Fe, Mn, and NO_3 also would be considered.

1.5. ADSORPTION AND EXCHANGE EQUILIBRIA

Models of surface chemical phenomena in GEOCHEM

The present state of understanding of surface chemical reactions in soils from the thermodynamic point of view is not nearly so advanced as in the cases of complexation, precipitation, and redox reactions. Currently, the surface behavior of cations and anions in soils is divided into two gross categories, adsorption and exchange, according to whether the surface reaction is considered to be largely irreversible or largely reversible, even though it is known that all adsorption processes involve the exchange of surface species and that many exchange processes are at least partly irreversible. As a general rule, adsorption phenomena tend to occur when relatively small concentrations of cations or anions interact with constant-potential surfaces and exchange phenomena tend to occur when ions interact with constant-change surfaces (Sposito, 1977; Stumm and Morgan, 1970). These generalizations are strictly empirical guides with many exceptions (e.g., ion exchange occurs on kaolinite which has only constant-potential surfaces and adsorption can occur on the constant-change surfaces of smectites). The classification of a particular soil surface reaction as adsorption or exchange is still a matter for individual discretion.

On a fundamental level, both adsorption and exchange processes concern the reactions of surface functional groups with ions and neutral molecules. Adsorption processes usually are those in which the functional groups display a very pronounced selectivity for one or more chemical species during a competitive exchange reaction. This selectivity can be expected to appear because the chemical bonds involved are more than simple interactions based on electrostatic or van der Waals forces. On the other hand, when the interactions do

TABLE 23. OUTPUT FROM THE SUBROUTINE OUTMAT FOR THE SYSTEM DESCRIBED IN TABLE 21

	FREE MET	CO3-	SO4	CL	PO4	CIT	SAL	PHTH	ARG	ORN	LYS
FREE LIG		6.78	2.86	2.29	10.51	16.54	11.74	4.30	7.38	11.27	11.57
CA	2.13	4.31	3.23	4.09	4.58	4.26	5.88	4.28	****	****	****
K	3.71	6.96	5.94	6.41	7.51	****	****	****	****	****	****
NA	3.01	5.96	5.04	5.51	6.76	****	****	****	****	****	****
FE3	14.90	5.47	14.55	12.93	8.40	4.84	8.63	****	13.18	17.07	****
FE2	13.24	13.81	14.44	15.88	14.72	13.18	17.83	****	17.10	21.19	19.99
MN	4.77	6.04	5.87	7.40	6.55	7.10	10.06	****	9.83	14.32	13.92
CU2+	8.20	7.18	9.21	10.37	9.61	5.75	8.79	8.86	7.69	12.35	17.35
CD	6.04	7.72	7.15	6.60	8.69	7.18	11.64	7.20	9.91	13.40	12.09
ZN	5.30	5.79	6.31	8.03	7.32	9.45	9.60	6.86	8.27	12.26	20.46
CU1+	16.81	****	****	16.03	****	****	****	****	****	****	****
HYDROGEN	6.30	2.71	7.40	17.07	4.14	6.18	4.28	5.34	4.49	4.36	4.36

TABLE 24. OUTPUT FROM OUTCST FOR REDOX DATA AND DESCRIPTION OF A SYSTEM BASED ON THE ANALYTICAL DATA IN TABLE 20

50	57	0	0	0	0	0	0	0	0	0	0	0	0	-144	0	1	1	0	0	0	0
50	60	0	0	0	0	0	0	0	0	0	0	0	0	608	0	1	1	793	0	1	2
50	61	0	0	0	0	0	0	0	0	0	0	0	0	65	0	1	1	0	0	0	0
50	99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

REDOX DATA	KRED	MREDOX	LREDOX	NELEC	NHRED	REDCST
	10	2	4	-8	8	1986

THESE COMPUTATIONS INVOLVE 9 METALS, 16 LIGANDS, 261 COMPLEXES AND 27 POSSIBLE SOLIDS.

IONIC STRENGTH = 0.4999999E-02

IONIC STRENGTH CORRECTIONS WILL BE PERFORMED

1 DIFFERENT CASES ARE TREATED

THE CONDITIONS FOR THE DIFFERENT CASES ARE

METAL	#INMAT	GUESS	TOTCC 1	LIGAND	#INMAT	GUESS	TOTCC 1
CA	1	4.000	2.070	CO3-	1	2.700	2.700
K	4	5.000	3.700	SO4	2	4.000	2.700
NA	5	4.500	3.000	CL	3	4.000	2.280
FE3	6	6.000	4.750	S	8	8.000	8.000
MN	8	6.000	4.700	PO4	9	5.000	4.000
CU2+	9	7.000	5.720	CIT	17	5.000	4.140
CD	11	6.000	5.850	SAL	19	5.000	4.270
ZN	12	6.500	5.130	PHTH	32	5.000	3.970
				ARG	33	5.000	4.490
				ORN	34	5.000	4.360
				LYS	35	5.000	4.360
				VAL	42	5.000	4.360
				NO3	57	3.500	2.170
				MAL	60	5.000	3.970
				BES	61	6.000	4.270

FIXED PH 6.300

REDOX POTENTIAL -2.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

SO4/S-2

TABLE 25. OUTPUT FROM THE SUBROUTINE OUT 1 FOR THE SYSTEM DESCRIBED IN TABLE 24

```
CASE NUMBER 1

NUMBER OF ITERATIONS = 35

SOLID CU2+ S     1 PRECIPITATES


NUMBER OF ITERATIONS = 38

SOLID CA   PO4     1 PRECIPITATES


NUMBER OF ITERATIONS = 41

SOLID CD   S     1 PRECIPITATES


NUMBER OF ITERATIONS = 43

SOLID ZN   S     1 PRECIPITATES


NUMBER OF ITERATIONS = 45


NUMBER OF ITERATIONS = 49


NUMBER OF ITERATIONS = 52


IONIC STRENGTH = 2.4808746E-02

FIXED PH = 6.300            COMPUTED TOTH = 0.3401679E-02

PE = -2.00
```

(Continued)

TABLE 25 (Continued)

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	7.3698163E-03	2.13254	8.5114017E-03	2.07000	-1.4697434E-09
K	1.9725425E-04	3.70497	1.9952665E-04	3.70000	-5.2346781E-12
NA	9.8547339E-04	3.00636	1.0000013E-03	3.00000	-8.0920243E-11
FE3	1.2128957E-15	14.91618	1.7782833E-05	4.75000	-3.2991432E-10
MN	1.7315775E-05	4.76156	1.9952669E-05	4.70000	-1.3001514E-11
CU2+	5.9628671E-18	17.22455	1.9054696E-06	5.72000	0.0
CD	1.4978361E-09	8.82454	1.4125435E-06	5.85000	0.0
ZN	1.4978292E-07	6.82454	7.4131376E-06	5.13000	0.0
CO3-	1.6811254E-07	6.77440	1.9952657E-03	2.70000	-1.3969839E-09
SO4	1.3949776E-03	2.85543	1.9952755E-03	2.70000	4.9658411E-10
CL	5.1650554E-03	2.28692	5.2480847E-03	2.28000	-3.4835639E-09
S	2.9144625E-18	17.53545	1.0506857E-05*	4.97853	4.9658411E-10
PO4	7.4286025E-13	12.12910	1.0000018E-04	4.00000	-1.4551915E-11
CIT	3.0047713E-17	16.52219	7.2443858E-05	4.14000	-1.0767214E-09
SAL	1.8158660E-12	11.74092	5.3703363E-05	4.27000	-1.3515944E-10
PHTH	5.0251023E-05	4.29886	1.0715231E-04	3.97000	-9.1784136E-11
ARG	4.1630070E-08	7.38059	3.2359472E-05	4.49000	3.5976666E-10
ORN	5.3539898E-12	11.27132	4.3651729E-05	4.36000	-1.1260681E-10
LYS	2.6873521E-12	11.57067	4.3651729E-05	4.36000	3.9426662E-10
VAL	2.2372259E-08	7.65029	4.3651729E-05	4.36000	3.1747049E-11
NO3	6.6293441E-03	2.17853	6.7608543E-03	2.17000	-1.4451293E-09
MAL	5.4094795E-05	4.26684	1.0715231E-04	3.97000	2.5220270E-11
BES	4.9842391E-05	4.30240	5.3703363E-05	4.27000	-6.6459338E-12

SOLID			MOLES PER LITER OF SOLUTION
CA	PO4	1	3.2534183E-05
CU2+	S	1	1.9054696E-06
CD	S	1	1.4101897E-06
ZN	S	1	7.1905833E-06

* Equal to the sum of concentrations of CdS, CuS, and ZnS.

primarily involve the charge and size characteristics of the reacting species, selectivities are less pronounced and the surface process should exhibit the reversibility feature associated with exchange phenomena.

Not enough is known about the surface functional groups and the nature of surface chemical bonds in soils to develop a comprehensive thermodynamic picture of adsorption and exchange reactions. Accordingly, the description of these reactions currently accepted is empirical and includes assumptions whose fundamental basis and degree of generality have not yet been established. This fact should be appreciated thoroughly when employing the two surface reaction models that are available in GEOCHEM. The characteristics of the particular problem the user of the program wishes to investigate should be examined carefully to delineate the possible limitations of the numerical results provided by GEOCHEM. In some cases the computations done by the program will be only of qualitative value and in others they may even be inappropriate.

Cation adsorption phenomena

GEOCHEM does not include a subroutine for anion adsorption, although provision for one has been made in columns 13-15 of Card No. 1. Cation adsorption reactions, e.g., the "specific adsorption" of Cu^{2+} by oxide surfaces, are described according to the semi-empirical model developed by James and Healy (1972). This paper should be read carefully before employing the program in a model calculation. (See also James et al., 1975, for some critical discussion of the model.) The James-Healy theory assumes that the total amount of metal adsorbed by a constant potential surface is the sum of the amounts of free metal cation and of all its known hydrolytic species on the surface. Each surface specie is considered to be in equilibrium with all other surface species and with the metal ions in solution, the equilibrium being governed by a conditional equilibrium constant that depends on the electrostatic, solvation, and non-coulombic interactions that occur. The data necessary in order to apply the model are the zero-point-of-charge pH value, dielectric constant, and total area of the adsorbing surface as well as the contribution to the Gibbs free energy of adsorption from non-coulombic interactions. The ZPC and area of the adsorbing surface can be determined experimentally by standard means (Stumm and Morgan, 1970). Typical estimates for the dielectric constant and the "chemical" part of the free energy of adsorption are $\varepsilon = 4.3$ and $\Delta G_{chem} = -12RT$, where R is the gas constant in kcal/mol ^{o}K, T is the absolute temperature in ^{o}K, and ΔG_{chem} is expressed in kcal/mol (James and Healy, 1972).

To include cation adsorption in a calculation performed by GEOCHEM, the number of different adsorbing surfaces (up to 5) is entered in columns 16-18 of Card No. 1 and three additional data cards are prepared.

Card No. 12. Format 5F10.5.

Card Columns	Type of Information
1-10	Enter the value of RT/F_y = 0.0252 J/C at 25°C
11-20	Enter the value of $eFy/16_{\pi\varepsilon_o}RT$ = 140 Å..
21-30	Enter the radius of H_2O = 1.38 Å..
31-40	Enter the dielectric constant of $H_2O(1)$ = 78.5 at 25°C.
41-50	Enter "1.0" (James-Healy "z" parameter)

The data entered on Card No. 12 are the values of parameters in the James-Healy model. R and T have their usual meanings; F_y is the Faraday constant, ε_o is the permitivity of free space, and e is the protonic charge. The paper of James and Healy (1972) should be consulted for details.

Card No. 13. Format 2I2, 13F5.2.

Card Columns	Type of Information
1-2	Code number of adsorbing surface (90-94)
3-4	Enter the total number of adsorbing metals.
5-9	Enter ZPC value for the surface.
10-14	Enter dielectric constant of the surface.
15-19	Enter a guess for -log "free" (i.e., without metal ions) adsorbing surface area in $10^4 m^2$/liter.
20-24	Enter -log total adsorbing surface area (for #90), in $10^4 m^2$/liter, for the first case.
25-29, etc.	Enter the same thing (for #90) for the second case, etc., up to 10 cases.

Card No. 13 is repeated for each different adsorbing surface, up to 5. The data entered in columns 15-19 are analogous to the estimate of free ionic concentration required in Card No. 4. The code numbers for adsorbing surfaces are listed in Table 1.

Card No. 14. Format 10(I2, F6.2).

Card Columns	Type of Information
1-2	Enter the code number of the first adsorbing metal (Table 1).

3-8	Enter the value of $\Delta G_{chem}/RT$ for the first adsorbing metal.
9-10, etc. 11-16, etc.	Repeat with data for the second adsorbing metal, up to 10 metals.

The code numbers for all of the metals on Card Nos. 3A, 3B, etc., must be entered on Card No. 14 in increasing numerical order (i.e., their order in Table 1). For each different adsorbing surface, a Card No. 14 is included directly after Card No. 13 for that surface. Some representative values of $\Delta G_{chem}/RT$ are given in Table I of the paper of James and Healy (1972).

Cation exchange equilibria

The exchange equilibrium model in GEOCHEM applies only to mono- and bivalent cations interacting with a montmorillonite surface. The thermodynamic data stored in the program refer to two representative clay minerals, Camp Berteau montmorillonite and Chambers bentonite. The Camp Berteau clay is an example of a smectite without isomorphous substitutions in the tetrahedral sheet whereas the Chambers bentonite has substitutions in both the tetrahedral and octahedral sheets. Some chemical data relating to these minerals is given in Table 26.

The cation exchange model has been described by Mattigod and Sposito (1979). It is based on three assumptions:

(1) The standard free energy of the reactions

$$HX(s,aq) = H^+(sq) + X^{-1}(s,aq) \quad (13)$$

$$NaX(s,aq) = Na^+(aq) + X^{-1}(s,aq) \quad (14)$$

is equal to zero, where (s,aq) denotes a homoionic montmorillonite or its anionic part in equilibrium with an aqueous electrolyte solution and X refers to one equivalent of the anionic part of the montmorillonite (see Table 26). This assumption implies that H- and Na-montmorillonite will be completely dissociated when they are in equilibrium with an infinitely dilute solution. It may be noted that Eq. (13) and (14) are analogous to the dissolution reaction of a solid and that the equilibrium constants for the reactions are analogous to solubility product constants.

(2) The standard free energy of formation of Na-montmorillonite may be calculated by the correlation technique of Mattigod and Sposito (1978).

(3) The activity coefficients of MX_m (M = metal cation of valence m) in a mixture of homoionic montmorillonites are always unity.

Assumptions (1) and (2) are sufficient to permit the computation of exchange equilibrium constants, since every exchange reaction can be

TABLE 26. CHEMICAL FORMULAS, FORMULA WEIGHTS, AND FORMATION CONSTANTS OF THE HOMOIONIC MONTMORILLONITES CONSIDERED IN GEOCHEM

Camp Berteau

$$X^{-1} = [(Al_{4.358}Fe^{3+}_{0.612}Fe^{2+}_{0.045}Mg_{0.955})Si_{11.94}O_{29.85}(OH)_{5.97}]^{-1}$$

Formula	Formula wt.	log K_M	Formula	Formula wt.	log K_M
NaX	1114.94	0	CuX_2	2247.44	11.61
KX	1131.05	1.41	ZnX_2	2249.27	8.27
MgX_2	2208.22	1.81	CdX_2	2296.30	10.67
CaX_2	2223.98	2.12	PbX_2	2391.09	21.09
NiX_2	2242.61	6.52			

Chambers

$$X^{-1} = [(Al_{2.891}Fe^{3+}_{0.467}Fe^{2+}_{0.016}Mg_{1.163})(Si_{8.304}Al_{0.391})O_{21.739}(OH)_{4.348}]^{-1}$$

Formula	Formula wt.	log K_M	Formula	Formula wt.	log K_M
NaX	821.77	0	CuX_2	1661.10	13.26
KX	837.88	1.04	ZnX_2	1662.93	9.85
MgX_2	1621.87	3.51	CdX_2	1709.96	11.95
CaX_2	1637.64	3.37	PbX_2	1804.75	22.01
NiX_2	1656.27	8.18			

written as a combination of two reactions like

$$m\ NaX(s,aq) + M^{+m}(aq) = MX_m(s,aq) + m\ Na^+(aq) \qquad (15)$$

with

$$\log K_{ex} = \frac{1}{5.707}\left[m\mu^o\ (NaX) + \mu^o\ (M^{+m}) - \mu^o\ (MX_m) - m\mu^o\ (Na^+)\right] \qquad (16)$$

at 25°C where μ^o is a standard free energy of formation in KJ/mol (Mattigod and Sposito, 1979). Assumption (3) states that homoionic clays will "precipitate" as independent solid phases, just as, e.g., $CaCO_3(s)$ and $AlPO_4(s)$ would be expected to do (and are assumed to do in GEOCHEM). There is experimental evidence supporting this assumption for Na^+-bivalent and bivalent-bivalent exchanges, but not for exchanges involving K^+. There are no data available that pertain to the multication exchanges (e.g., Na^+, K^+, Ca^{2+}, and Mg^{2+} simultaneously) that are typical in natural soil solutions.

Assumptions (1) to (3) make it possible to regard cation exchange as a kind of precipitation-dissolution reaction. Accordingly, the homoionic montmorillonite MX_m is treated the same as an ordinary solid in GEOCHEM, in that formation constants for $MX_m(s,aq)$ are stored in the program (see Table 26) and X (either Camp Berteau or Chambers) is regarded as a solid-forming ligand. However, X (= CBER or CHAM) is assigned zero charge in GEOCHEM in order that it not contribute to the calculated ionic strength nor receive an activity coefficient computed according to the Davies equation.

In order to include cation exchange in a computation performed by GEOCHEM, one need only enter a total concentration of CBER or CHAM (in mol/liter) on a ligand card as described for ordinary solids in subsection 1.3. A corresponding set of total metal concentrations should also be entered on the appropriate cards in order to maintain electrical neutrality. The procedure may be understood by studying the following example computation.

<u>An example: Adsorption and exchange of Cd in an acid, montmorillonitic soil</u>.

Table 27 lists analytical data needed by GEOCHEM in order to predict the fate of $CdSO_4$ added to make a concentration of 10^{-6} M in the aqueous phase of a water-saturated San Miguel soil (Typic Natrixeralf, coarse-loamy, montmorillonitic, thermic). The Camp Berteau montmorillonite was chosen as a model for the clay fraction in this soil, insofar as cation exchange is concerned.

The total concentration of montmorillonite anion may be calculated from the expression:

TABLE 27. ANALYTICAL DATA FOR A SAN MIGUEL SOIL SOLUTION

Component	pC	Component	pC
Ca	0.78*(2.58)	CO_3	3.70
Mg	0.78*(2.61)	SO_4	2.30
K	3.10	Cl	2.39
Na	2.52	CBER	0.18
Cd	6.00	pH	5.60

* Due to assignment of one-half $MONT_T$ to CaX_2 or MgX_2, where X = CBER: $MONT_T = 2\ CaX_2 + 2\ MgX_2 = 0.66\ \underline{M}$.

$$MONT_T = CEC/S \qquad (MONT_T \text{ in mol/liter}) \qquad (17)$$

where CEC is the cation exchange capacity of the soil in meq/gm soil and S is the gravimetric water content of the soil at saturation. The assumptions underlying Eq. (17) are that the clay fraction is entirely montmorillonite and accounts for all the cation exchange capacity of the soil and that the analytical data to be used as input to the program refer to a saturation extract. An additional, tacit assumption is that the aqueous phase which resides in the volume occupied by the whole soil is in contact with all of the clay fraction of that volume. In the case of the San Miguel soil, CEC = 0.177 meq/gm soil and S = 0.27 gm H_2O/gm soil, so $MONT_T = 0.66\ \underline{M}$. One-half of this concentration was assigned each to the Ca and Mg forms of the clay, as indicated in Table 27.

The total area of adsorbing surface may be estimated using the equation:

$$A_T = Sp \times \%\ \text{adsorbent} \times 10/S \qquad (A_T \text{ in } m^2/\text{liter}) \qquad (18)$$

where Sp is the specific surface of the adsorbent in m^2/gm and % adsorbent is its weight percentage in the soil. In the present example, the product Sp x % adsorbent was taken equal to 12.1 m^2/gm soil. The ZPC and dielectric constant of the adsorbent were set at 2.0 and 4.3, respectively. The values chosen for $\Delta G_{chem}/RT$ were -0.1 (Na), -0.1(K), -8(Mg), -10(Ca), and -12(Cd).

Table 28 shows the output from the subroutine OUTCST for this problem. The data entered on Card No. 12 are listed under the heading "Adsorption Data" along with the chosen values of ZPC and the adsorbent

TABLE 28. OUTPUT FROM THE SUBROUTINE OUTCST FOR THE DATA IN TABLE 27.

ADSORPTION DATA

XRTF = 0.02520
XENPI = 140.00000
Rh = 1.38000
EPSBUL = 78.50000
ZEL = 1.00000

SURFACE	PZC	EPSOL
90	2.00	4.30

INPUT DATA FOR VERIFICATION

MET	LIG *	SOLID				COMPLEXES											
1	1	791	1 1 0	0	0 0 0	0	0 0 0	271	1 1 0	1094	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0
1	2	411	1 1 0	0	0 0 0	0	0 0 0	181	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	3	0	0 0 0	0	0 0 0	0	0 0 0	35	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	63	186	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
1	90	0	0 0 0	0	0 0 0	0	0 0 0	5	126 0	-9	126-1	0	0 0 0	0	0 0 0	0	0 0 0
1	99	-2318	1 0-2	0	0 0 0	0	0 0 0	-1275	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	1	461	1 1 0	699	5 4-2	0	0 0 0	241	1 1 0	1084	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0
2	2	0	0 0 0	0	0 0 0	0	0 0 0	171	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	3	0	0 0 0	0	0 0 0	0	0 0 0	25	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	63	156	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
2	90	0	0 0 0	0	0 0 0	0	0 0 0	4	122 0	-10	122-1	16	422-4	0	0 0 0	0	0 0 0
2	99	-1688	1 0-2	0	0 0 0	0	0 0 0	-1195	1 0-1	-3957	4 0-4	0	0 0 0	0	0 0 0	0	0 0 0
4	1	0	0 0 0	0	0 0 0	0	0 0 0	65	1 1 0	986	1 1 1	33	2 1 0	0	0 0 0	0	0 0 0
4	2	0	0 0 0	0	0 0 0	0	0 0 0	65	1 1 0	156	1 1 1	113	2 1 0	0	0 0 0	0	0 0 0
4	3	0	0 0 0	0	0 0 0	0	0 0 0	-42	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	63	134	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
4	90	0	0 0 0	0	0 0 0	0	0 0 0	6	131 0	3	131-1	0	0 0 0	0	0 0 0	0	0 0 0
4	99	0	0 0 0	0	0 0 0	0	0 0 0	-1453	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	1	93	2 1 0	0	0 0 0	0	0 0 0	35	1 1 0	1016	1 1 1	-106	2 1 0	0	0 0 0	0	0 0 0
5	2	0	0 0 0	0	0 0 0	0	0 0 0	85	1 1 0	166	1 1 1	113	2 1 0	0	0 0 0	0	0 0 0
5	3	0	0 0 0	0	0 0 0	0	0 0 0	-22	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	63	-5	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
5	90	0	0 0 0	0	0 0 0	0	0 0 0	5	126 0	2	126-1	0	0 0 0	0	0 0 0	0	0 0 0
5	99	0	0 0 0	0	0 0 0	0	0 0 0	-1423	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
11	1	1151	1 1 0	0	0 0 0	0	0 0 0	361	1 1 0	411	1 2 0	1144	1 1 1	0	0 0 0	0	0 0 0
11	2	0	0 0 0	0	0 0 0	0	0 0 0	181	1 1 0	241	1 2 0	190	1 3 0	244	1 1 1	0	0 0 0
11	3	0	0 0 0	0	0 0 0	0	0 0 0	175	1 1 0	223	1 2 0	203	1 3 0	145	1 4 0	-877	1 1-1
11	63	1046	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
11	90	0	0 0 0	0	0 0 0	0	0 0 0	5	126 0	-9	126-1	-13	126-2	-3	126-3	17	126-4
11	99	-1388	1 0-2	0	0 0 0	0	0 0 0	-1025	1 0-1	-2058	1 0-2	-3339	1 0-3	-4727	1 0-4	-930	2 0-1
50	1	1789	0 1 2	0	0 0 0	0	0 0 0	1008	0 1 1	1639	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0
50	2	0	0 0 0	0	0 0 0	0	0 0 0	178	0 1 1	-860	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0
50	3	0	0 0 0	0	0 0 0	0	0 0 0	-849	0 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	63	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	90	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
50	99	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0

dielectric constant. The formation constants (at ionic strength 0.0201 M) for the solids Ca-, Mg-, Na-, K-, Cd-, and H-montmorillonite are listed under "solid" in the usual way. Table 29 shows the output for the subroutine OUT 1. In this commputation, all solids were allowed and the ionic strength was fixed at the value computed by GEOCHEM for the San Miguel soil solution in the absence of exchangeable cations and adsorbing surfaces. The values of pC for Ca and Mg in this reference soil solution are given in parentheses in Table 26. By employing the reference ionic strength, one is assuming that only solution species contribute to the ionic strength; the exchangeable cations are excluded. Table 29 gives the values of 2.303 $\Delta G_{ads}/RT$ and its component free energies for each metal and metal hydrolytic species that can be adsorbed (see James and Healy, 1972, for details concerning G_{coul}, G_{solv}, and G_{chem}). Table 30 shows the output from OUT138. It may be noted that Cd is predicted to become entirely exchangeable, while Ca is partly adsorbed and partly exchangeable. The fact that about two-thirds of the added concentration of montmorillonite is predicted to be free ligand should be interpreted in the light of the log K values in Table 26. "Free ligand" means that the neutralizing cations are in the same state as Na^+ on Na-montmorillonite, since log K for that solid has been set equal to zero. If log K for Na-clay were chosen to be a positive quantity instead, then the values of log K for the bivalent exchangeable cations would be augmented by 2 log K_{Na} and a greater "precipitation" of Ca-, and Mg-montmorillonite would be predicted than what appears in Table 30.

1.6. OPEN SYSTEMS

GEOCHEM can calculate the equilibrium speciation and set of solid phases in a soil solution that is free to exchange CO_2 and N_2 with the soil atmosphere. An exchange of O_2 with the soil atmosphere also can be treated indirectly by adjustment of the pE value, since

$$\log p_{O_2} = -83.1 + 4pH + 4pE \qquad (19)$$

where p_{O_2} is the partial pressure of O_2 in atmospheres (Stumm and Morgan, 1970, p. 309). If the soil atmosphere is in equilibrium with the terrestrial surface atmosphere, $p_{CO_2} = 10^{-3.5}$ atm. and $p_{N_2} = 10^{-0.1}$ atm. Otherwise, the partial pressures of CO_2 and N_2 may be adjusted in the input data to fit the soil conditions which prevail.

For convenience in computation, CO_2 and N_2 are manipulated in the same way as are solid phases in the program. CO_2 will be listed as "solid" H_2CO_3 and N_2 will be listed as "solid" $H_{12}(NO_3)_2$ in the outputs from the subroutines OUTCST, OUT 1, and OUT 138. There is no provision for O_2 as a "solid" in the program. In order to prescribe an equilibrium with a given partial pressure of this gas, Eq. (19) must be solved for the corresponding pE value (at a given pH value) and a redox computation must be performed as described in subsection 1.4.

TABLE 29. OUTPUT FROM OUT 1 FOR THE DATA DESCRIBED IN TABLE 27.

ADSORPTION CONSTANTS

CONSTANTS FOR ADSORPTION ON SURFACE ADSI

METAL	LOGK (X100) 1	2	3	4	5	6	GCOUL 1	2	3	4	5	6	GSOLV 1	2	3	4	5	6	GCHEM
CA	-29	-963	*****	*****	*****	*****	-9.1	-4.6	*****	*****	*****	*****	16.5	4.1	*****	*****	*****	*****	-10.0
MG	-165	-974	-6080	*****	*****	*****	-9.4	-4.7	-18.8	*****	*****	*****	18.1	4.5	72.5	*****	*****	*****	-8.0
NA	-117	-1598	*****	*****	*****	*****	-4.4	0.0	*****	*****	*****	*****	3.8	0.0	*****	*****	*****	*****	-0.1
K	-119	-1560	*****	*****	*****	*****	-4.6	0.0	*****	*****	*****	*****	4.2	0.0	*****	*****	*****	*****	-0.1
CD	54	-626	-1677	-3337	-5465	-1579	-9.1	-4.6	0.0	4.6	9.1	-13.7	16.6	4.2	0.0	4.2	16.6	37.4	-12.0

NUMBER OF ITERATIONS = 4

SOLID CD CBER 1 PRECIPITATES

NUMBER OF ITERATIONS = 76

SOLID CA CBER 1 PERCIPITATES

NUMBER OF ITERATIONS = 9

SOLID MG CBER 1 PRECIPITATES

NUMBER OF ITERATIONS = 12

IONIC STRENGTH = 2.0099998E-02

FIXED PH = 5.600 COMPUTED TOTH = 0.3384664E-03

	FREE CONC	LOG FREE CONC	TOT CONC	LOG TOT CONC	REMAINDER
CA	7.1585715E-02	1.14517	1.6595882E-01	0.78000	0.0
MG	1.4283228E-01	0.84517	1.6595882E-01	0.78000	0.0
K	7.0000547E-04	3.10188	7.0433038E-04	3.10000	-8.0924531E-11
NA	3.0020922E-03	2.52258	3.0199585E-03	2.52000	-1.1300884E-10
CD	1.7981876E-10	9.74517	1.0000031E-06	6.00000	0.0
CO3-	8.8378727E-10	9.05365	1.9952655E-04	3.70000	-2.9103830E-11
SO4	3.8637361E-04	3.41299	5.0118901E-03	2.30000	2.8110065E-07
CL	2.8762678E-03	2.54117	4.0738136E-03	2.39000	3.7164256E-08
CBER	4.3912405E-01	0.35741	6.6069365E-01	0.18000	-1.1336995E-05
ADS1	2.1982737E-02	1.65792	4.4668481E-02	1.35000	4.4393590E-07

SOLID		MOLES PER LITER OF SOLUTION
CA	CBER	9.1305017E-02
MG	CBER	1.9473113E-02
CD	CBER	9.9977206E-07

TABLE 30. OUTPUT FROM OUT138 FOR THE DATA IN TABLE 27

```
PRIMARY DISTRIBUTION OF METALS AND LIGANDS

CA
    AS A FREE METAL/   43.1 PERCENT
    BOUND WITH SO4-/    1.1 PERCENT
    BOUND WITH CL  /    0.3 PERCENT
    IN SOLID FORM WITH CBER/ 55.0 PERCENT
    BOUND WITH ADSI/    0.5 PERCENT
MG
    AS A FREE METAL/   86.1 PERCENT
    BOUND WITH SO4 /    1.7 PERCENT
    BOUND WITH CI  /    0.4 PERCENT
    IN SOLID FORM WITH CBER/ 11.7 PERCENT
K
    AS A FREE METAL/   99.6 PERCENT
    BOUND WITH SO4 /    0.2 PERCENT
    BOUND WITH CL  /    0.1 PERCENT
    BOUND WITH ADSI/    0.1 PERCENT
NA
    AS A FREE METAL/   99.4 PERCENT
    BOUND WITH SO4 /    0.3 PERCENT
    BOUND WITH CL  /    0.2 PERCENT
    BOUND WITH ADSI/    0.1 PERCENT
CD
    IN SOLID FORM WITH CBER/100.0 PERCENT
CO3-
    BOUND WITH CA  /    7.0 PERCENT
    BOUND WITH MG  /   11.0 PERCENT
    BOUND WITH H   /   82.0 PERCENT
SO4
    AS A FREE LIGAND/   7.7 PERCENT
    BOUND WITH CA  /   35.6 PERCENT
    BOUND WITH MG  /   56.5 PERCENT
    BOUND WITH NA       0.2 PERCENT
CL
    AS A FREE LIGAND/  70.6 PERCENT
    BOUND WITH CA  /   11.3 PERCENT
    BOUND WITH MG  /   17.9 PERCENT
    BOUND WITH NA  /    0.1 PERCENT
CBER
    AS A FREE LIGAND/  66.5 PERCENT
    IN SOLID FORM WITH CA  / 27.6 PERCENT
    IN SOLID FORM WITH MG  /  5.9 PERCENT
ADSI
    AS A FREE LIGAND/  49.2 PERCENT
    BOUND WITH CA  /   47.0 PERCENT
    BOUND WITH MG  /    3.5 PERCENT
    BOUND WITH NA  /    0.2 PERCENT
```

In order to introduce $CO_2(g)$ as a component in the system, there is a need only to enter CO_3 as one of the ligands and to prepare Card No. 6 as follows:

Card No. 6. Format 10F5.2

Card Columns	Type of Information
1-5	Enter the value of -log p_{CO_2} for the first set of concentration data.
6-10, etc.	Repeat the procedure for the second case, etc., up to 10. If "0" is entered at any point, the preceding value of -log p_{CO_2} is understood. For example, a 3.5 in columns 1-5 followed by "0" in columns 6-10, 11-15, and 16-20 means -log p_{CO_2} = 3.5 for cases 1, 2, 3, and 4.

The value of p_{CO_2} and the pH value are sufficient to determine the carbonate equilibrium in any open soil solution, even when complexes form between CO_3^{2-}, H^+, and the metal cations in the system. Therefore, the value of -log CO_{3T} entered on the carbonate ligand card is redundant chemically. However, it is required computationally in order to avoid the situation where H_2CO_3 "dissolves" (i.e., $CO_2(g)$ disappears into the atmosphere) during the iterations. If this happens, it means that not enough total carbonate was put into the system to maintain an equilibrium with the imposed partial pressure of CO_2. Accordingly, it is important that the value of -log CO_{3T} entered be small enough to allow the speciation of carbonate to occur as well as equilibrium with the atmosphere. As a rule, -log CO_{3T} = 1.0 should be sufficiently small, but the value chosen is arbitrary. If the concentration of carbonate imposed is in excess, the program will report that H_2CO_3 "precipitates", meaning that the excess CO_2 has escaped to the atmosphere. This does not affect the value of P_{CO_2} imposed because the atmosphere is a CO_2 reservoir and it does not alter the carbonate speciation because that depends only on pH and p_{CO_2}.

In some cases a soil solution is in equilibrium with CO_2 at a partial pressure that is greater than $10^{-3.5}$ atm. and the value of CO_{3T} can be determined rapidly enough after extraction of the solution that it represents an input concentration for the system that is chemically significant and not arbitrary. For this situation it is the value of p_{CO_2} that should be adjusted while that of CO_{3T} is maintained on the carbonate ligand card at the measured value. The most straightforward procedure is to run the analytical data as several cases in the calculation by GEOCHEM, with the only difference among the cases being in the value of -log p_{CO_2} on Card No. 6. Those values of -log p_{CO_2} that result in H_2CO_3 "dissolving" are too large for the system. The largest

value of -log p_{CO_2} that results in H_2CO_3 "precipitating" is the one that equals the true equilibrium value. This value usually can be determined by trial and error after running a few cases. The resulting speciation and solid phase composition calculated by GEOCHEM then represent equilibrium for the soil solution under the value of p_{CO_2} deduced.

If a soil solution is free to exchange N_2 with its surroundings, chemical effects can be expected only if redox equilibria are considered, since the aqueous species of nitrogen contain N in oxidation states different from zero. Therefore, in order to include an imposed N_2 partial pressure in an equilibrium calculation performed by GEOCHEM, the procedures described in section 4 must be followed. Card Nos. 7 and 10 must be included along with a ligand card for NO_3 and Card No. 8 must be prepared as follows:

Card No. 8. Format 10F5.2

Card Columns	Type of Information
1-5	Enter the value of -log p_{N_2} for the first set of concentration data.
6-10, etc.	Repeat the procedure for the second case, etc., up to 10. If "0" is entered at any point, then the preceding value of -log p_{N_2} is understood.

The value of p_{N_2} will almost always be $10^{-0.1}$ atm. It is important once again to prevent the gas phase from escaping ($H_{12}(NO_3)_6$ "dissolves") during the calculation by imposing a small enough value of -log NO_{3T} in the nitrate ligand card. If there is some reason to believe that the value of NO_{3T} should be fixed during the computation, then -log p_{N_2} can be adjusted in trial-and-error runs, as described for CO_2.

1.7 INTERACTION INTENSITIES AND CAPACITIES

In a complicated, multicomponent chemical system such as a soil solution, it is necessary to employ a computer program like GEOCHEM in order to account in detail for the many reactions that occur. For each set of concentration data that describes a given soil solution, the speciation of the components and the array of solid phases to be found at equilibrium are summarized in a detailed fashion by the percentage distribution tables printed as the output from the subroutine OUT 138. Often it is desired to learn how the percentage distribution will shift in response to changes in pH, pE, CO_2 partial pressure, or the total concentrations of certain components of a soil solution. In this case, several runs of GEOCHEM can be made for the different imposed conditions and the output from OUT 138 can be examined for trends.

An alternative to a case-by-case examination of percentage distribution figures is the computation of interaction intensities and capacities. These quantities are defined expressly for the purpose of elucidating the principal pathways of interaction in a multicomponent chemical system. The interaction capacity for a pair of components, X, Y, is defined by the expression:

$$\delta'_{X,Y} = \frac{\partial pX}{\partial TOTY} \tag{20}$$

where pX = -log [X], [X] is the molar free ionic concentration of component X, and TOTY is the total molar concentration of component Y. The partial derivative in Eq. (7.1) is carried out with all components but X and Y held at a fixed total concentration. The well known pH buffer capacity is a special case of an interaction capacity:

$$\beta_H = \frac{TOTH}{pH} = 1/\delta'_{H,H} \tag{21}$$

Except for H, the value of TOTY for any metal or ligand component in a soil solution will be a non-negative number. This fact makes it possible to define a dimensionless quantity called the interaction intensity of two components X and Y:

$$\delta_{H,Y} = \frac{\partial\ pX}{\partial pTOTY} \tag{22}$$

where pTOTY is the negative common logarithm of the total concentration of component Y ($Y \neq H$) in the system. Clearly

$$\delta_{X,Y} = -2.303TOTY\ \delta'_{X,Y} \tag{23}$$

for any component $Y \neq H$.

The concepts of interaction intensities and capacities have been discussed at length with many examples by Morel et al. (1973, 1976). As a general rule, a large absolute value of $\delta_{X,Y}$ corresponds to a very great dependence of the free ionic concentration of X on the total concentration of Y in the system. If $\delta_{X,Y} > 0$ and large, the free ionic concentration of X increases greatly when the amount of Y in the system increases. If $\delta_{X,Y} < 0$ and its absolute value is large, the free ionic concentration of X drops significantly when the amount of Y increases. If $\delta_{X,Y} \simeq 0$, the presence of Y in the system has little effect on the chemistry of X. By examining a table of interaction intensities for a given set or sets of analytical data, one can usually identify quite directly the major interaction webs among the components of a soil solution. Often most of the values of $\delta_{X,Y}$ will be very small and the principal set of components that determines the chemical fate of a chosen metal or ligand X can be established almost at a glance. Several examples of tables of $\delta_{X,Y}$ values are presented by Morel et al. (1973, 1976) and Ingle et al. (1978).

As an illustration of the application of interaction intensities, Fig. 1 shows a plot of the absolute value of $\delta_{Cd,Y}$ against pH for an aqueous solution containing the metals and ligands listed in Table 31. The data shown in Fig. 1 were adapted directly from Morel et al. (1973). For pH values below 6.2, where $CdCO_3(s)$ does not precipitate, the concentration of Cd^{2+} depends almost entirely on the total concentration of Cd in the system, with some considerably smaller dependence on the total concentrations of complexing ligands such as Cl^- and SO_4^{2-}. The dependence of $[Cd^{2+}]$ on Ca is not large and comes principally through the effect of Ca on sulfate and carbonate ligands. Above pH 6.2, $CdCO_3(s)$ precipitates in the system and $\delta_{Cd,CO_3} = -1$ until $CaCO_3(s)$ precipitates at pH 8.4. The values of $\delta_{Cd,Cd}$ and $\delta_{Cd,Cl}$ now decrease considerably and $\delta_{Cd,Ca}$ grows as the Ca present titrates the CO_3^{2-} which increases with the pH value.

TABLE 31. THE SYSTEM CONSIDERED IN RELATION TO FIG. 1

Metal	pC	Metal	pC	Ligand	pC
Ca	3.00	Zn	7.00	CO_3	3.00
Mg	3.50	Ni	6.50	SO_4	4.50
Na	3.50	Hg	9.00	Cl	3.50
Fe	5.00	Pb	7.00	F	5.50
Mn	5.50	Co	7.50	NH_3	5.50
Cu	6.00	Ag	9.00	PO_4	5.00
Ba	7.00	Al	5.00	SiO_3	4.00
Cd	6.00	H	--	OH	--

The interaction capacities can be used to compute approximate changes in pX following small changes in a Y component. As an example, the use of interaction capacities to compute pH has been illustrated by Morel et al. (1976).

Interaction intensities and capacities are computed by GEOCHEM if the appropriate entries are made on Card No. 1. In card columns 31-33, a "0" entered means "no interaction intensities or capacities are computed", a "1" entered means "compute and print interaction capacities", and a "2" entered means "compute and print interaction intensities", and a "3" entered means "compute and print both interaction intensities

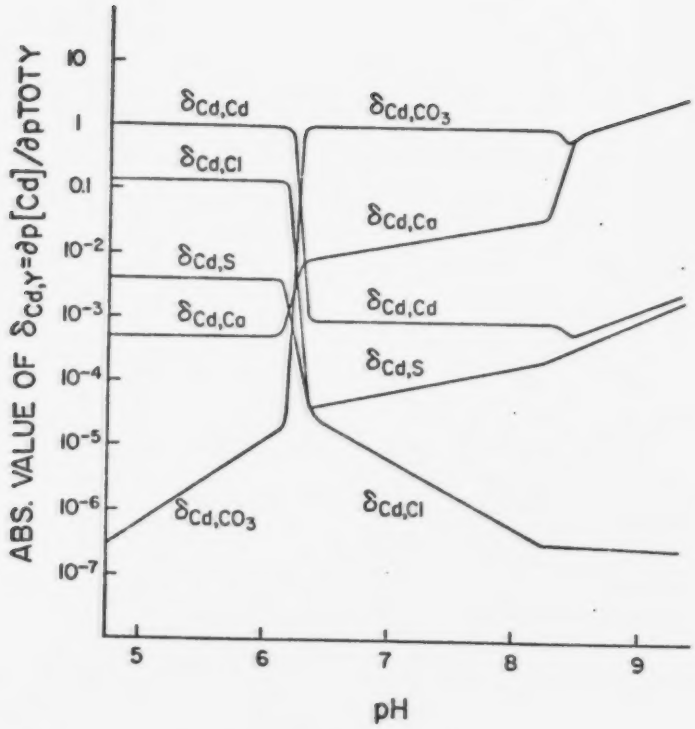

Fig. 1. A graph of the absolute value of $\delta_{Cd,Y}$ versus pH for the system described in Table 31 (after Morel et al. (1973).

and capacities. The subroutine OUTJAC computes and prints these quantities. Note that $\delta_{X,H}^{*}$ is always printed instead of $\delta_{X,H}$, even if a"2" is entered. OUTJAC prints components X vertically and components Y horizontally in the table of $\delta_{X,Y}^{*}$ or $\delta_{X,Y}$ values. Typical output of $\delta_{X,Y}^{*}$ and $\delta_{X,Y}$ values are shown in Table 32 for the system in Table 31 at a pH value of 6.0.

1.8. THE THERMODYNAMIC DATA IN GEOCHEM

The thermodynamic data file

The thermodynamic data stored in GEOCHEM are thermodynamic equilibrium constants and stoichiometric coefficients for soluble complexes, solids, and redox couples. These data have been compiled with a great deal of care, but they should be reviewed frequently and compared to new data on reactions of interest that appear in the chemical, geochemical, and soil chemical literature. Useful critical compilations, such as those by Martell and Smith (1976-77), Baes and Mesmer (1976), and Robie et al. (1978) should be consulted often. It is very important to keep in mind that the calculational results produced by GEOCHEM can never be any better than the thermodynamic data it contains. A brief discussion of the methodologies involved in selecting thermodynamic equilibrium constants has been given by Sposito and Mattigod (1977).

At present GEOCHEM can store up to six thermodynamic stability constants for soluble complexes and up to three thermodynamic formation constants for solids for each possible metal-ligand combination. These maximal numbers have not been reached for many of the combinations as yet, so much more data can be added. To examine the data file in GEOCHEM, one should have it printed out; control cards to print data stored on disc in an IBM 360/50 system are shown in Table 33. These cards may require modification for other computing systems. If the data file is to be modified, it should be punched onto cards using the appropriate control cards. The data deck produced in this way is described in the next section.

Adding new thermodynamic data

Modifications of the existing thermodynamic equilibrium constants in GEOCHEM or the addition of equilibrium constants for metal-ligand combinations not already in the program can be accomplished by preparing a new thermodynamic data deck and transferring it to the disc storage location accessed by GEOCHEM when it performs a calculation. The control cards that transfer the data deck should be developed in consultation with the user's computer center. The data deck that comes after these control cards has the following structure:

INTERACTION CAPACITIES:

	CA	MG	NA	FE3	MN	CU2+	BA	CD	ZN	NI	HG	PB
CA	-4.34E 02	-1.43E-01	-1.43E-02	-1.38E 01	-2.92E-01	-3.77E 00	-1.49E-01	-2.21E-01	-7.00E-01	-1.18E 00	-5.52E 00	-2.00E 00
MG	-1.43E-01	-1.37E 03	-1.17E-02	-1.20E 01	-2.58E-01	-3.23E 00	-1.19E-01	-1.82E-01	-6.52E-01	-1.00E 00	-4.7[illegible]E 00	-2.49E 00
NA	-1.43E-02	-1.17E-02	-1.57E 03	-1.80E 00	-2.70E-02	-5.02E-01	-1.19E-02	-2.40E-02	-9.10E-02	-1.51E-01	-8.82E-01	-3.76E-01
FE3	-1.38E 01	-1.20E 01	-1.80E 00	-1.82E 04	-1.08E 02	-3.53E 03	5.44E-03	-4.04E 01	-5.53E 02	-1.01E 03	-5.28E 03	-2.00E 03
MN	-2.92E-01	-2.58E-01	-2.70E-02	-1.08E 02	-1.57E 05	-2.93E 01	-1.48E-01	-3.01E-01	-9.81E 00	-8.47E 00	-3.23E 01	-2.10E 01
CU2+	-3.77E 00	-3.20E 00	-5.02E-01	-3.53E 03	-2.93E 01	-4.35E 05	-3.29E-02	-1.12E 01	-1.53E 02	-2.74E 02	-1.03E 03	-7.10E 02
BA	-1.49E-01	-1.19E-01	-1.19E-02	5.43E-03	-1.48E-01	-3.29E-02	-4.34E 06	-1.50E-01	-1.64E-01	-1.15E-01	-3.02E-01	-1.24E-01
CD	-2.21E-01	-1.82E-01	-2.40E-02	-4.04E 01	-5.01E-01	-1.12E 01	-1.50E-01	-4.34E 05	-1.92E 00	-3.20E 00	-4.73E 01	-1.42E 00
ZN	-7.00E-01	-6.52E-01	-9.10E-02	-5.53E 02	-4.81E 00	-1.53E 02	-1.04E-01	-1.92E 00	-4.34E 06	-4.27E 01	-1.64E 04	-1.15E 02
NI	-1.18E 00	-1.00E 00	-1.51E-01	-1.01E 03	-8.47E 00	-2.74E 02	-1.15E-01	-3.20E 00	-4.37E 01	-1.37E 06	-2.98E 02	-2.64E 02
HG	-8.52E 00	-3.94E 00	-8.32E-01	-5.38E 03	-3.24E 01	-1.04E 03	-3.03E-01	-3.03E 01	-1.04E 04	-2.98E 04	-4.24E 06	-7.48E 04
PB	-2.00E 00	-2.45E 00	-3.70E-01	-2.08E 03	-2.16E 01	-7.10E 02	-1.27E-01	-8.42E 00	-1.13E 02	-2.04E 02	-7.99E 02	-4.34E 06
CO3+	-1.38E 01	-1.20E 01	-1.80E 00	-1.82E 04	-1.06E 02	-3.53E 03	5.44E-03	-4.04E 01	-5.53E 02	-1.01E 03	-5.38E 03	-2.08E 03
AG	-3.53E-01	-2.01E-01	-8.38E-02	-5.10E-02	-7.94E-02	-5.15E-02	-8.11E-02	-8.43E 00	-6.23E-02	-3.03E-02	-4.08E 02	-1.51E 00
AL	-1.38E 01	-1.20E 01	-1.80E 00	-1.82E 04	-1.06E 02	-3.53E 03	5.39E-03	-4.04E 01	-5.53E 02	-1.11E 03	-5.38E 03	-2.08E 03
CO3-	5.05E 00	7.74E 00	1.20E 03	1.03E 04	7.10E 01	2.35E 03	-2.47E-03	2.08E 01	3.08E 02	6.04E 02	3.04E 03	1.75E 03
SO4	4.50E 01	5.58E 01	3.60E 00	2.33E 00	4.40E 01	1.05E 01	4.51E 01	4.37E 01	4.45E 01	3.40E 01	8.75E-01	5.43E 01
CL	1.30E 00	1.03E 00	3.13E-01	7.73E-02	2.66E-01	1.46E-01	2.72E-01	3.17E 01	1.94E-01	1.13E-01	1.53E 03	5.84E 00
F	3.22E 03	2.01E 01	1.28E-02	4.92E 01	3.29E-01	1.07E 01	6.40E-01	4.00E 00	7.04E 00	5.02E 00	1.46E 01	1.00E 01
NH3	4.59E 00	3.49E 00	6.00E-01	6.05E 03	3.60E 01	1.22E 03	-1.61E-03	1.30E 01	1.04E 02	3.30E 02	1.79E 03	6.92E 02
PO4	2.93E 01	3.48E 01	1.45E 00	1.15E 04	1.45E 02	2.25E 03	1.94E 00	3.02E 01	3.91E 02	6.56E 02	3.40E 03	1.71E 03
SIO3	9.18E 00	7.99E 00	1.20E 03	1.21E 04	7.40E 01	2.35E 03	-3.57E-03	2.70E 01	3.69E 02	6.72E 02	3.59E 03	1.78E 03
H	-4.59E 00	-4.00E 00	-6.01E-01	-6.06E 03	-3.60E 01	-1.18E 03	1.81E-03	-1.35E 01	-1.04E 02	-3.30E 02	-1.79E 03	-8.42E 02

(To provide the reader with complete information, this computer printout has been included. These are the best copies available; we regret that that portions are undecipherable.)

TABLE 32. OUTPUT FROM THE SUBROUTINE OUTJAC FOR THE SYSTEM DESCRIBED IN TABLE 31.

Reproduced from best available copy.

	CO3+	AG	AL	CO3-	SO4	CL	F	NH3	PO4	SiO3	H
CA	-1.38E 01	-3.53E-01	-1.30E 01	9.05E 00	4.50E 01	1.30E 00	3.22E 00	4.59E 00	2.93E 01	9.16E 00	-4.59E 00
MG	-1.23E 01	-2.81E-01	-1.20E 01	7.70E 00	3.54E 01	1.02E 00	2.01E 01	3.94E 00	3.45E 01	7.95E 00	-4.00E 00
NA	-1.00E 00	-6.38E-02	-1.00E 00	1.20E 00	3.00E 00	3.13E-01	1.26E-02	6.03E-01	1.03E 00	1.20E 00	-6.01E-01
FE3	-1.02E 04	-5.43E-02	-1.02E 04	1.03E 04	2.33E 00	7.73E-02	4.92E 01	6.05E 03	1.15E 04	1.21E 04	-6.00E 03
MN	-1.08E 02	-7.95E-02	-1.06E 02	7.10E 01	4.40E 01	2.65E-01	3.29E-01	3.60E 00	1.95E 02	7.20E 01	-3.00E 01
CU2+	-3.53E 03	-5.09E-02	-3.53E 03	2.35E 03	1.05E 01	1.62E-01	1.07E 01	1.22E 03	2.25E 03	2.35E 03	-1.18E 03
BA	5.43E-03	-6.11E-02	5.37E-03	-2.47E-03	4.51E 01	2.72E-01	6.40E-01	-1.00E-03	1.99E 00	-3.56E-03	1.01E-03
CD	-4.04E 01	-8.43E 00	-4.34E 01	2.68E 01	4.37E 01	3.17E 01	4.00E 00	1.36E 01	3.02E 01	2.70E 01	-1.35E 01
ZN	-5.53E 02	-6.20E-02	-5.53E 02	3.68E 02	4.95E 01	1.94E-01	7.64E 00	1.84E 02	3.91E 02	3.68E 02	-1.84E 02
NI	-1.01E 03	-3.85E-02	-1.01E 03	6.69E 02	3.48E 01	1.13E-01	5.02E 00	3.36E 02	6.50E 02	6.70E 02	-3.36E 02
MG	-5.38E 03	-1.31E 02	-5.38E 03	3.04E 03	7.56E-01	1.49E 03	1.49E 01	1.79E 03	3.40E 03	3.54E 03	-1.79E 03
PB	-2.68E 03	-1.51E 00	-2.66E 03	1.75E 03	3.93E 01	5.84E 00	1.00E 01	8.92E 02	1.71E 03	1.70E 03	-8.92E 02
CO3+	-1.02E 04	-5.43E-02	-1.02E 04	1.03E 04	2.33E 00	7.73E-02	4.92E 01	6.05E 03	1.15E 04	1.21E 04	-6.00E 03
AG	-5.18E-02	-4.34E 00	-5.14E-02	3.07E-02	2.70E 00	3.65E 02	8.91E-03	5.14E-01	5.94E-02	3.05E-02	-1.73E-02
AL	-1.02E 04	-5.57E-02	-2.33E 04	1.03E 04	2.33E 00	7.67E-02	8.08E 01	6.03E 03	1.15E 04	1.04E 04	-6.00E 03
CO3-	1.03E 04	3.31E-02	1.03E 04	-6.22E 03	-1.49E 00	-4.54E-02	-2.78E 01	-3.42E 03	-6.47E 03	-6.04E 03	3.42E 03
SO4	2.33E 00	2.73E 00	2.33E 00	-1.49E 00	-1.37E 04	-1.65E-01	-8.59E-01	-7.79E-01	-4.35E 00	-1.50E 00	7.60E-01
CL	7.73E-02	3.65E 02	7.73E-02	-4.90E-02	-1.65E-01	-1.37E 03	-2.51E-02	-2.54E-04	-1.32E-01	-5.15E-02	2.00E-02
F	4.92E 01	8.92E-03	6.06E 01	-2.78E 01	-8.59E-01	-2.51E-02	-1.37E 03	-1.84E 01	-3.10E 01	-4.44E 01	1.44E 01
NH3	6.05E 03	5.15E-01	6.05E 03	-3.42E 03	-7.79E-01	-2.54E-02	-1.84E 01	-1.34E 03	-3.82E 03	-4.03E 03	2.02E 03
PO4	1.15E 04	5.79E-02	1.15E 04	-6.47E 03	-4.35E 00	-1.32E-01	-3.10E 01	-3.82E 03	-5.07E 04	-7.03E 03	3.02E 03
SiO3	1.21E 04	3.70E-02	1.09E 04	-6.04E 03	-1.50E 00	-5.15E-02	-4.44E 01	-4.03E 03	-7.03E 03	-1.15E 04	4.04E 03
H	-6.00E 03	-1.01E-02	-6.00E 03	3.42E 03	7.60E-01	2.57E-02	1.04E 01	2.02E 03	3.02E 03	4.04E 03	-2.02E 03

(To provide the reader with complete information, this computer printout has been included. These are the best copies available; we regret that that portions are undecipherable.)

TABLE 32. continued.

INTERACTION INTENSITIES:

	CA	MG	NA	FE3	MN	CU2+	GA	CD	ZN	NI	HG	PB
CA	1.00E 00	1.04E-04	1.04E-05	5.17E-04	4.13E-06	6.66E-06	3.43E-06	5.10E-07	1.76E-07	6.02E-07	1.27E-08	6.03E-07
MG	3.30E-06	1.00E 00	6.45E-06	2.76E-04	1.88E-06	7.38E-06	2.74E-06	4.19E-07	1.50E-07	7.32E-07	1.08E-08	5.64E-07
NA	3.30E-05	8.49E-06	1.00E 00	4.15E-05	2.62E-07	1.16E-06	2.73E-09	5.65E-06	4.11E-08	1.10E-07	2.03E-09	8.30E-08
FE3	3.17E-02	6.73E-03	1.31E-03	4.19E-01	7.87E-04	6.13E-03	-1.25E-09	9.31E-05	1.27E-04	7.34E-04	1.24E-05	6.17E-04
MN	6.73E-06	1.68E-04	2.02E-05	2.45E-03	1.00E 00	6.73E-05	3.41E-08	1.15E-06	1.11E-06	6.17E-06	7.43E-08	4.54E-06
CU2+	6.08E-05	2.53E-03	3.66E-04	6.13E-02	2.14E-04	1.00E 00	7.58E-05	2.57E-05	3.53E-05	2.03E-04	2.41E-06	1.05E-04
GA	3.43E-06	6.07E-05	8.66E-06	-1.25E-07	1.08E-06	7.52E-08	1.00E 00	3.46E-07	3.78E-08	6.36E-08	6.95E-10	2.58E-08
CD	5.10E-04	1.33E-04	1.79E-05	9.31E-04	3.65E-06	2.57E-05	3.46E-08	1.00E 00	4.41E-07	2.34E-06	1.04E-07	1.44E-06
ZN	1.76E-05	4.74E-04	6.69E-05	1.27E-02	3.51E-05	3.53E-04	3.78E-08	4.41E-06	1.00E 00	3.19E-05	3.77E-07	2.59E-05
NI	2.73E-03	7.32E-04	1.10E-04	2.32E-02	6.17E-05	6.41E-04	2.64E-08	7.50E-06	1.01E-05	1.00E 00	6.07E-07	4.71E-05
HG	1.04E-02	2.87E-03	3.64E-04	1.24E-01	2.36E-04	2.41E-03	8.40E-08	6.98E-05	3.77E-05	2.17E-04	1.00E 00	1.84E-04
PB	6.63E-03	1.78E-03	2.75E-04	6.17E-02	1.58E-04	1.65E-03	2.98E-08	1.94E-05	2.59E-05	1.49E-04	1.84E-06	1.00E 00
CD3+	3.17E-02	6.73E-03	1.31E-03	4.19E-01	7.87E-04	6.13E-03	-1.25E-09	9.31E-05	1.27E-04	7.34E-04	1.24E-05	6.17E-04
AG	6.13E-04	2.04E-04	6.13E-05	1.19E-06	5.79E-07	1.16E-07	1.67E-08	1.94E-05	1.43E-06	2.79E-08	5.55E-07	3.46E-07
AL	3.17E-02	6.73E-03	1.31E-03	4.19E-01	7.87E-04	6.13E-03	-1.24E-09	9.31E-05	1.27E-04	7.34E-04	1.24E-05	6.16E-04
CO3-	-2.08E-02	-5.67E-03	-6.73E-04	-2.36E-01	-5.17E-04	-5.41E-03	5.69E-10	-6.17E-05	-8.47E-05	-4.87E-04	-8.59E-06	-4.03E-04
SO4	-1.04E-01	-2.60E-02	-2.62E-03	-5.38E-05	-3.21E-04	-2.42E-05	-1.04E-05	-1.01E-04	-1.14E-05	-2.54E-05	-2.01E-09	-9.66E-06
CL	-2.94E-03	-7.51E-04	-2.26E-04	-1.78E-06	-1.94E-06	-3.75E-07	-6.27E-08	-7.30E-05	-4.47E-08	-6.20E-08	-3.52E-06	-1.20E-06
F	-7.41E-03	-1.47E-02	-9.33E-06	-1.13E-03	-2.40E-06	-2.46E-05	-1.47E-07	-9.22E-06	-1.62E-06	-4.24E-06	-3.36E-08	-2.31E-06
NH3	-1.06E-02	-2.91E-03	-4.37E-04	-1.39E-01	-2.62E-04	-2.81E-03	4.17E-10	-3.13E-05	-4.24E-05	-2.45E-04	-4.13E-06	-2.05E-04
PO4	-6.75E-02	-2.54E-02	-1.35E-03	-2.64E-01	-1.06E-03	-5.14E-03	-4.59E-07	-8.80E-05	-9.01E-05	-4.79E-04	-7.82E-06	-3.54E-04
SIO3	-2.11E-02	-5.82E-03	-6.75E-04	-2.79E-01	-5.24E-04	-5.42E-03	8.23E-10	-6.21E-05	-8.49E-05	-4.89E-04	-8.26E-06	-4.11E-04
H	1.06E-02	2.91E-03	4.38E-04	1.40E-01	2.62E-04	2.71E-03	-4.14E-10	3.10E-05	4.25E-05	2.45E-04	4.13E-06	2.06E-04

(To provide the reader with complete information, this computer printout has been included. These are the best copies available; we regret that that portions are undecipherable.)

TABLE 32. continued.

	CO3+	AG	AL	CO3-	SO4	CL	F	NH3	PO4	SIO3	H
CA	1.00E-04	8.13E-10	3.17E-04	-2.08E-02	-3.27E-03	-9.44E-04	-2.34E-05	-3.34E-05	-8.75E-04	-2.11E-03	-4.59E 00
MG	8.73E-07	6.47E-10	2.76E-04	-1.79E-02	-2.60E-03	-7.51E-04	-1.47E-04	-2.91E-05	-8.02E-04	-1.84E-03	-4.00E 00
NA	1.31E-07	1.93E-10	4.15E-05	-2.76E-03	-2.62E-04	-2.26E-04	-9.33E-08	-4.37E-06	-4.26E-05	-2.77E-04	-6.01E-01
FE3	1.32E-03	1.25E-10	4.19E-01	-2.36E 01	-1.70E-04	-5.61E-05	-3.58E-04	-4.41E-02	-2.64E-01	-2.79E 00	-6.06E 03
MN	7.87E-06	1.83E-10	2.49E-03	-1.64E-01	-3.21E-03	-1.54E-04	-2.40E-06	-2.62E-04	-3.34E-03	-1.66E-02	-3.60E 01
CU2+	2.57E-04	1.17E-10	8.13E-02	-5.41E 00	-7.65E-04	-1.18E-04	-7.70E-05	-8.50E-03	-5.10E-02	-5.42E-01	-1.18E 03
SR	-3.96E-10	1.87E-10	-1.24E-07	5.66E-06	-3.29E-03	-1.58E-04	-4.66E-08	1.31E-08	-4.59E-05	8.20E-07	1.81E-03
CO	2.95E-08	1.54E-08	9.31E-04	-6.17E-02	-3.18E-03	-2.31E-02	-2.91E-05	-9.90E-05	-6.80E-04	-6.21E-03	-1.35E 01
ZN	4.03E-05	1.43E-10	1.27E-02	-8.47E-01	-3.60E-03	-1.41E-04	-5.12E-05	-1.34E-03	-9.01E-03	-8.45E-02	-1.84E 02
NI	7.34E-05	8.87E-11	2.32E-02	-1.54E 00	-2.54E-03	-8.20E-05	-4.24E-05	-2.45E-03	-1.52E-02	-1.55E-01	-3.36E 02
MO	3.92E-04	3.01E-07	1.24E-01	-8.99E 00	-5.51E-05	-1.09E 00	-1.06E-04	-1.30E-02	-7.82E-02	-8.26E-01	-1.79E 03
PB	1.95E-04	3.48E-09	6.16E-02	-4.03E 00	-2.86E-03	-4.11E-03	-7.29E-05	-6.49E-03	-3.94E-02	-4.11E-01	-8.92E 02
CO3+	1.32E-03	1.25E-10	4.19E-01	-2.36E 01	-1.70E-04	-5.61E-05	-3.58E-04	-4.41E-02	-2.64E-01	-2.79E 00	-6.06E 03
AG	3.77E-09	1.00E 00	1.19E-06	-7.07E-05	-1.97E-04	-2.65E-01	-5.03E-08	-3.74E-06	-1.28E-06	-7.96E-06	-1.73E-02
AL	1.32E-03	1.28E-10	5.29E-01	-2.36E 01	-1.70E-04	-5.58E-05	-4.42E-04	-4.41E-02	-2.64E-01	-3.90E 00	-6.06E 03
CO3-	-7.47E-04	-7.63E-11	-2.36E-01	1.43E 01	1.09E-04	3.60E-05	2.02E-04	2.49E-02	1.49E-01	1.57E 00	3.42E 03
SO4	-1.73E-07	-6.23E-09	-5.36E-05	3.44E-03	1.00E 00	1.23E-04	6.26E-06	5.67E-06	1.00E-04	3.56E-04	7.78E-01
CL	-5.63E-09	-6.43E-07	-1.76E-06	1.13E-04	1.20E-05	1.00E 00	1.83E-07	1.88E-07	3.04E-06	1.19E-05	2.56E-02
F	-3.58E-06	-1.59E-11	-1.40E-03	8.40E-02	6.26E-05	1.83E-05	9.96E-01	1.19E-04	7.28E-04	1.02E-02	1.04E 01
NH3	-4.41E-04	-1.15E-09	-1.39E-01	7.87E 00	5.67E-05	1.88E-05	1.19E-04	1.01E 00	6.80E-02	9.29E-01	2.02E 03
PO4	-8.36E-04	-1.33E-10	-2.64E-01	1.49E 01	3.17E-04	9.59E-05	2.30E-04	2.78E-02	1.17E 00	1.76E 00	3.82E 03
SIO3	-8.02E-04	-8.67E-11	-3.90E-01	1.57E 01	1.13E-04	3.71E-05	3.23E-04	2.94E-02	1.76E-01	2.97E 00	4.04E 03
H	4.41E-04	4.17E-11	1.40E-01	-7.87E 00	-5.67E-05	-1.87E-05	-1.19E-04	-1.47E-02	-8.81E-02	-9.30E-01	-2.02E 03

(To provide the reader with complete information, this computer printout has been included. These are the best copies available; we regret that that portions are undecipherable.)

TABLE 32. continued.

Table 33. CONTROL CARDS FOR PRINTING THE THERMODYNAMIC DATA FILE IN GEOCHEM

IBM FORTRAN Coding Form GX28-7327-6 U/M 050** Printed in U.S.A.

```
DISCPRIN JOB
      EXEC FORTGCLG
FORT.SYSIN DD *
      DIMENSION ALPHA(20)
   10 READ(2,100,END=99) ALPHA
      WRITE(6,200) ALPHA
      GO TO 10
   99 STOP
  100 FORMAT(20A4)
  200 FORMAT(2X,20A4)
      END
GO.FT02F001 DD DSN=C1509.DATA,DISP=SHR,UNIT=2314,VOL=SER=USR003
```

Card No.	Format	Card Col.	Type of Information Entered
1	2I3	1-3	Total number of metals in the data file, including H^+
		4-6	Total number of ligands in the data file, including OH^-

Note: According to Table 1, there are 36 metals and 65 ligands considered by the program. There also are 14 metal "slots" and 29 ligand "slots" available for new components. If new metals and ligands are being added, they should be accounted for in Card No. 1. The metal code numbers available are 36 to 49; the available ligand code numbers are 65 to 89 and 95 to 98. The code symbols for the metals are M36, M37, etc., and those for the ligands are L65, L66, etc.

2	I2,I3, F7.2	1-2	Code number of metal (Table 1)
		3-5	Valence of metal
		6-12	Ionic radius of metal, in Å

Note: Card No. 2 is repeated for every metal considered by the program. The ordering of the metal cards must be the same as in Table 1.

3	I2,I3, F7.2	1-2	Code number of ligand (Table 1)
		3-5	Valence of ligand, including sign
		6-12	Ionic radius of ligand, in Å

Note: Card No. 3 is repeated for every ligand considered by the program, in the proper order. New components are described in Card Nos. 2 and 3 in the same way as existing components. Their cards are placed last.

4	I5,F5.2, F5.1	1-5	Number of metal-ligand combinations considered by the program
		6-10	Value of -log K_w (enter "14")
		11-15	Value of -10 log K for the reaction:

$$2H^+ + CO_3^{2-} = CO_2(g) + H_2O$$

(enter "182.0")

Note: At present GEOCHEM considers 986 metal-ligand combinations. The data on Card No. 4 may be altered if new complexes and solids are to be added or if better values of K_w and K become available.

5	2I2, 9(I4, 2I1, I2)	1-2	Code number of metal (Table 1)
		3-4	Code number of ligand combined with metal (Table 1).
		5-8	Value of 10 log K for solid No. 1
		9	Stoichiometric coefficient of metal in solid

Card No.	Format	Card Col.	Type of Information Entered
		10	Stoichiometric coefficient of ligand in solid
		11-12	Stoichiometric coefficient of H or OH in solid (negative for OH, zero if no H or OH present)
		13-16	Value of 10 log K for solid No. 2
		17, 18, 19-20	Same as for columns 9, 10, 11-12
		21-24	Same as for columns 5-8, 9, 10, 11-12
		25, 26, 27-28	
		29-32	Value of 10 log K for complex No. 1
		33	Stoichiometric coefficient of metal in complex
		34	Stoichiometric coefficient of ligand in complex
		35-36	Stoichiometric coefficient of H or OH in complex (< 0 for OH, "0" if no H or OH present)
		37-40	This sequence is repeated for each complex formed by the metal-ligand combination, up to 6 in total
		41	
		42	
		43-44	

Note: The thermodynamic equilibrium constant for a solid is defined in Subsection 1.3 and that for a complex is defined in Subsection 1.2. in GEOCHEM, K for a solid equals the inverse of the solubility product constant and K for a complex equals the stability constant. Card No. 5 is repeated for every metal-ligand combination considered by the program, except HOH.

6	I5	1-5	Number of redox reactions considered by the program, up to 30 (24 presently in GEOCHEM)
7	9I5, A8	1-5	Redox reaction No. from Table 3
		6-10	Code number of reactant metal or ligand (Tables 1 and 3, column M)
		11-15	Code number of product metal or ligand, or of second reactant metal or ligand if a complex or solid is formed (Tables 1 and 3, column L)
		16-20	+10 if two ligands involved, +9 to +1 if a metal-ligand complex is involved, -1 to -9 if a solid is involved, -10 if two metals involved (Table 3, "Reaction Type")
		21-25	Value of NE (Tables 3 and 19)

Card No.	Format	Card Col.	Type of Information Entered
		26-30	Value of NH (Tables 3 and 19)
		31-35	Value of 10 log K (Table 3)
		36-40	Stoichiometric coefficient of specie entered in col. 6-10 (Enter "0" if ± 10 was entered in col. 16-20 or if the species is H^+. See column CM in Table 3)
		41-45	Stoichiometric coefficient of specie entered in col. 11-15 (Enter "0" if ± 10 was entered in col. 16-20 or if the specie is OH^-. See column CL in Table 3)
		46-53	Alphanumeric name of reaction (Table 3)

Note: Card No. 7 is repeated for each redox reaction considered by the program. The last reaction entered must be $2\ NO_3^- + 12\ H^+ = N_2(g) + 6\ H_2O - 10\ e$.

8	I4	1-4	Number of mixed solids considered (presently 14)
9	11I4, I6, 2I3, A8	1-4	Code number of mixed solid (Table 2)
		5-8	Reaction code: "0" if solid contains up to 2 metals and 2 ligands besides H or OH; "1" if solid contains up to 4 metals besides Al^{3+} and $SiO_2(OH)_2^{2-}$
		9-12	Code number of first metal (Table 1)
		13-16	Code number of second metal (Enter 50 if no second metal)
		17-20	Code number of third metal or first ligand, or "50"
		21-24	Code number of fourth metal or "50", or second ligand or "99"
		25-28 29-32 33-36 37-40	Stoichiometric coefficients of the species entered in col. 9-12, 13-16, 17-20, and 21-24. Enter "0" if specie is not present in the solid
		41-44	Number of H or OH in the solid (negative for OH). Do not count OH in $SiO_2(OH)_2^{2-}$
		45-50	Value of 10 log K, where K = equilibrium constant for the formation of the solid
		51-53	Number of Al^{3+} in solid
		54-56	Number of $SiO_2(OH)_2^{2-}$ in solid
		57-64	Alphanumeric name of the solid (Table ")

1.9 ERROR MESSAGES GENERATED BY GEOCHEM

There are four error messages that are generated by the program when the data to be analyzed have not been specified properly. A listing of these error messages and the steps to take when they occur follow.

(1) BE CAREFUL NO CONVERGENCE.

This message will be generated whenever 500 iterations have been exceeded as the program attempts to solve the set of mole balance equations for the data under consideration. There are two principal causes for lack of convergence:

(a) If a large set of solid phases is precipitated during the computation, or simply for very large computations, the system may be converging although more iterations are required. In this case the remainders shown in the output from OUT 1 will be smaller than the total concentrations used as the input data. To correct, run the computation again using the free concentrations shown in OUT 1 as the guesses and imposing the precipitated solids listed there and no others. Alternatively, the number of iterations can be increased by inserting the following card immediately before Card No. 1. (See Card 0, Subsection 1.1).

ITMAX Card. Format I3, 5X, E14.8.

Card Columns	Type of Information
1-3	Enter the maximum number of iterations permitted.
4-8	Blank
9-22	Enter the convergence criterion, i.e., the maximum value of EPS, where EPS = calculated total conc. - input total conc. ÷ input total conc.

(b) If the system has diverged, this can be ascertained by inspecting the values of the remainders in the table of free and total concentrations for the specific case. The remainder, R, is the difference between the computed and imposed analytical concentrations. If $|R|$/ TOTX < EPS, specified on the ITMAX Card, the system is considered to be converged. Thus, by comparing the remainders and total concentrations, the problem areas of the computation may be identified. Further information can be obtained from this listing of complex concentrations produced by OUT 17. By hand computation on the problem subsystem, better input guesses of the free concentrations can be obtained. To correct, run again with better guesses of the free ionic concentrations and/or a different value of EPS.

There are two general situations in which convergence problems may be expected:

(1) If both a metal M and a ligand L are nearly all bound in a strong complex C (i.e., $^{c}K = [C]/[M][L]$ is very large) and the total concentration of the metal is approximately the same as the total concentration of the ligand. For example, $^{c}K = 10^{20}$, [C] 10^{-2} M total concentration of metal = total concentration of ligand, then $[M] = [L] = 10^{-11}$ M. But the mass-action equation is also satisfied within the precision of the program when $[M] = 10^{-13}$ M and $[L] = 10^{-9}$ M.

(2) If a solid is precipitated in very small amounts. For example, suppose that the total concentration of $Ca^{2+} = 10^{-1}$ M, the total concentration of $PO_4^{3-} = 10^{-8}$ M, and solid $Ca_5(PO_4)_3OH$ is present. Very small changes in the concentration of either Ca^{2+} or PO_4^{3-} can give very different solubility results because of the large stoichiometric coefficients in this solid.

(2) ERROR RETURN FROM GAUSSL DIAGONAL TERM REDUCED TO ZERO.

GAUSSL is the name of a Gaussian elimination subroutine which solves the system of nonliner mole balance equations. This error message will be generated if one of the diagonal elements of the computational matrix becomes equal to zero. It is not likely that this will happen if the input data have been specified properly. To correct, check the input concentration data for errors.

(3) REPEATED PRECIPITATION DISSOLUTION.

Under some circumstances the program will precipitate a solid phase and then dissolve it, repeatedly. It is likely, when this occurs, that another solid with the same metal-ligand combination should be precipitated instead. To correct, restart the computation with the suspected correct solid imposed.

(4) GIBBS PHASE RULE VIOLATED IN SUBSYSTEM.

This error message will be generated when a solid set is imposed which is inconsistent with Gibbs Phase Rule. As discussed in section 1.3, the program requires two degrees of freedom (T, P) in order to choose the equilibrium constants. To correct, restart the computation with a set of imposed solids consistent with the phase rule, if too many were imposed initially, or with a set suspected to be correct, but not generated correctly by the program as the result of the order of precipitation. (The first condition is the more likely).

The fact that, during a multi-case computation, the preceding case is used as a guess for the next case may also cause phase rule problems. When solids are precipitated in a preceding case, those solids are imposed on the next case and, if pE, pH or some other parameter is radically different between the two cases, those solids probably should not be imposed.

SECTION 2

FRACTIONATION OF SLUDGES

2.1. PROPERTIES OF THE FULVIC ACID FRACTION

Analytical properties

An understanding of the mechanisms through which sewage sludges incorporated in soil form water-soluble complexes with trace metals should provide a basis for the prediction and control of potentially harmful levels of enrichment of these metals in the soil solution. In view of the existent literature on metal complexation by components of natural soil organic matter (Schnitzer and Khan, 1972), it is reasonable to suggest that the fulvic acid fraction of sludge-amended soil will play an important role in determining this expected enhancement in trace metal solubility. The fulvic acid fraction of natural soil organic matter has been shown to be especially reactive towards trace metal cations and has the important defining property of being water soluble in the range of pH normally encountered in soil solutions.

The fulvic acid fractions of three representative sludge-soil mixtures were extracted, purified, and then studied for their analytical properties. The fulvic acids extracted from sewage sludge (SS fulvic acids) were found to contain from 20 to 40 times as much S as a typical fulvic acid extracted from natural soil organic matter (SOM fulvic acid). Two of the SS fulvic acids also had somewhat less O than a typical SOM fulvic acid. Ultraviolet and visible spectra of the SS fulvic acids suggested that they may be highly aromatic materials and that they may have condensed structures, comparable even with those in SOM humic acids, in those cases where the O content is relatively low. The aromatic nature of the SS fulvic acids could be inferred indirectly from their X-ray diffraction patterns, which yielded a -band centered more nearly at 4Å than 5Å, thus implying a relatively small content of aliphatic components.

The infrared spectra of the SS fulvic acids were generally similar to the type III spectrum of SOM fulvic acid:* The absorption due to

---

* Type I spectra are characteristic of soil humic acids, Type II spectra are characteristic of the low-molecular weight fraction of SOM fulfic acids, and Type III spectra are characteristic of SOM fulvic acids (Stevenson and Goh, 1971).

C = O in carboxyl groups is not pronounced and the presence of polysaccharides and protein decomposition products is indicated. The spectra differed importantly from the Type III spectrum in showing bands due to the sulfonyl group and to functional groups substituted on aromatic rings.

The elemental composition of the SS fulvic acids is presented in Table 34 together with the ranges of the percentages of C, H, N, O, and S that have been reported for SOM fulvic acids extracted from soils in many parts of the world (Kononova, 1966; Stevenson and Goh, 1971;

Table 34. ULTIMATE ANALYSES* OF SS FULVIC ACIDS COMPARED WITH THOSE OF SOM FULVIC ACIDS.

	SS fulvic acid			SOM fulvic acids
	A	B1	C	
C	30.3 ± 1.7†	45.2 ± 3.0	46.95 ± .84	40-55
H	5.20 ± .16	7.31 ± .28	7.21 ± .05	1.5-7.0
N	1.77 ± .18	3.06 ± .06	3.67 ± .14	.7-3.5
O‡	51.1	40.0	35.7	39-50
S	11.56 ± .95	4.46 ± .65	8.44 ± .42	.1-3.6

* Percentage, water- and ash-free basis.

† Mean deviation computed on data for three different samples of fulvic acid.

‡ Calculated by difference: % O = 100 - % (C+H+N+S).

Griffith and Schnitzer, 1975). The percentages of P in the SS fulvic acids were found to be 0.34 ± 0.03, 1.83 ± 0.04, and 2.13 ± 0.06, respectively, for sludge designated A, B1, and C (determination in triplicate). These rather low figures are not included in Table 34. because they are comparable with the ash contents of the SS fulvic acids and, therefore, may not represent P in an organic form. The SS fulvic acid ash has a large percentage of metal phosphate (Holtzclaw et al.,1976) and must contribute an important fraction of the P determined in the fulvic acid. If some of this P actually were in organic form, the figures for percent O in Table 34 would be reduced correspondingly by small amounts. The composition of the SS fulvic acids differs from that

of SOM fulvic acids in a major respect: SS fulvic acid contains a very high percentage of S. The S content of fulvic acid A, for example, is about 40 times that found typically in a SOM fulvic acid. In order to check whether this figure was in some way an artifact of the particular analytical procedure used to determine sulfate after oxidation of the fulvic acid sample in the Parr bomb, the percentage of S in fulvic acid A was determined by two other accepted (although less convenient) methods. These were a colorimetric technique that utilizes barium chloranilate (Bertolacini and Barney, 1957; Beaton et al., 1968) and a titrimetric method utilizing $CaCl_2$ in an acetone-water mixture (Chapman and Pratt, 1961, p. 189f). The results of the three different determinations of S for one sample of fulvic acid A produced data in close agreement, thus supporting the accuracy of the % S figures in Table 34.

The principal conclusions to be drawn from the data in Table 34. are that SS fulvic acids can show significant variability in their chemical compositions, but that S-containing components should exert an important influence on their chemistry in any case. In connection with variability, it is of interest to note that fulvic acid A appears to contain S at the expense of C (by comparison with SOM fulvic acids), whereas fulvic acids B1 and C appear to contain sulfur at the expense of O. Indeed, the rather low % O figures for fulvic acids B1 and C are similar to those characteristic of SOM humic acids (Schnitzer and Khan, 1972, p. 30). The implication here, then, is that functional groups such as, for example, sulfonyls and sulfhydryls, will play an important role in SS fulvic acids and that relatively condensed structures related to those in SOM humic acids may perhaps be found in some SS fulvic acids as well. Experiments to determine quantitatively the S-containing components of SS fulvic acids would be necessary before further progress can be expected in elucidating the structural chemistry of these materials.

The UV-visible spectra of the SS fulvic acids are shown in Fig. 2. These spectra are very similar to the UV-visible spectra of SOM fulvic acids in that they are generally featureless. However, in the alkaline $NaHCO_3$ solution, they do show a weak absorption at about 265 nm. The ratio of extinction coefficients at 465 nm and 665 nm, E_4/E_6 was found to have the values 7.0, 4.7, and 5.9 for fulvic acids from sludges designated as A, B1, and C, respectively. The solution of fulvic acid A was diluted twofold and threefold and still yielded the same value of E_4/E_6. This concentration independence of the ratio is expected for any humic material if the Lambert-Beer law is valid (Schnitzer and Khan, when compared with the typical range for SOM fulvic acids, 6.0 to 10.0 (Schnitzer and Khan, 1972, p. 59). In fact, values near 5 are at the upper limit of the range of E_4/E_6 for SOM humic acids. This fact suggests that, in accordance with the usual interpretation of E_4/E_6 data, the degree of molecular complexity in fulvic acids B1 and C may be comparable to what is expected in SOM humic acids. On the other hand, the value of 7.0 for E_4/E_6 in the case of fulvic acid A implies that A possesses a relatively more open molecular structure and one that is more characteristic of SOM fulvic acids. These inferences are in agreement with the implications of the elemental composition data. The significance of the absorption at 265 nm in the UV spectra of the SS

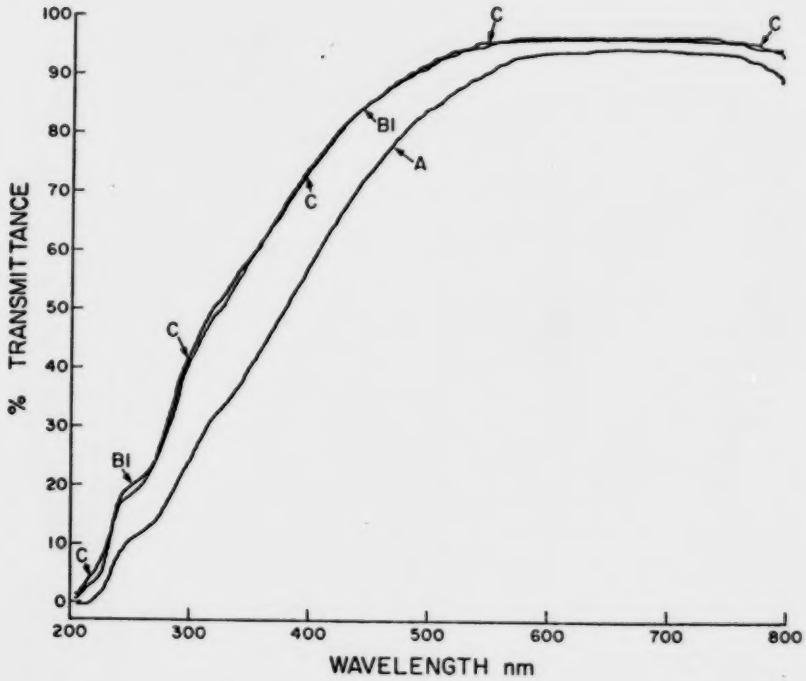

Figure 2. The UV-visible spectra of SS fulvic acids, A, Bl, and C.

suggests that, in accordance with the usual interpretation of E_4/E_6 data, the degree of molecular complexity in fulvic acids B1 and C may be comparable to what is expected in SOM humic acids. On the other hand, the value of 7.0 for E_4/E_6 in the case of fulvic acid A implies that A possesses a relatively more open molecular structure and one that is more characteristic of SOM fulvic acids. These inferences are in agreement with the implications of the elemental composition data. The significance of the absorption at 265 nm in the UV spectra of the SS fulvic acids is not completely apparent. It is possible that this absorption simply points to a significant aromatic character in these materials, since a peak at 265 nm has been observed in highly aromatic fractions isolated from SOM fulvic and humic acids (Schnitzer and Skinner, 1968; Khan and Schnitzer, 1971).

The X-ray diffraction patterns for the SS fulvic acids (not shown) exhibited only a broad maximum near 4Å and otherwise were characteristic of X-ray amorphous, carbonaceous materials. The diffraction maximum near 4Å (the so-called γ-band) is supposed to arise from an irregular packing of condensed aromatic layers normal to their planes. The irregularity is produced by the interference of aliphatic edge groups around the aromatic units (Schnitzer and Khan, 1972, p. 91). The fact that the maximum was observed to appear nearer to 4Å than to 5Å suggests that much of the C in the SS fulvic acids is indeed in condensed aromatic "nuclei" instead of side chains.

Infrared spectra of the SS fulvic acids are reproduced in Fig. 3. The principal features of the spectra are very similar to those in the Type III spectra of SOM fulvic acids (Stevenson and Goh, 1971). An example of a Type III spectrum (labeled D) is also shown in Fig. 3 and may be used as the basis for making band assignments (Stevenson and Butler, 1969; Stevenson and Goh, 1971). These are given in Table 35. The most important common features of the SS fulvic acid spectra and the Type III spectrum are: (i) a fairly weak absorption at 2940 cm^{-1} due to aliphatic CH_2 and CH_3, (ii) a pair of relatively similar absorption bands at 1720 cm^{-1} and 1650 cm^{-1}, due to C=O in carbonyl and in amide groups, respectively, and (iii) rather pronounced absorption bands at 1540 cm^{-1} and 1050 cm^{-1}, due to amide groups in peptide linkages of proteins and to C-O stretching in polysaccharides, respectively. The most important differences between the SS fulvic acid spectra and the Type III spectrum are: (i) the deep absorption at 1160 cm^{-1} and the shoulder absorption at 1360 cm^{-1}, along with the broad, deep band between 1160 cm^{-1} and 1200 cm^{-1}, and (ii) the narrow absorption bands at 880 cm^{-1} and 580 cm^{-1}, in the SS fulvic acid spectra.

The bands at 1670 cm^{-1} and 1540 cm^{-1} do not appear in the spectrum of fulvic acid A. This result may be understood in terms of the correlation between N content and absorbance at 1540 cm^{-1} determined by Ishiwatari (1970) for humic acids. The threshold N content for the first appearance of the amide II band was found to be about 2%; thereafter, the absorbance increased linearly with % N. This effect can be seen in Fig. 3. Fulvic acid A (1.8% N) produces no amide II band, while fulvic acids B1 and C do show this band in pro-

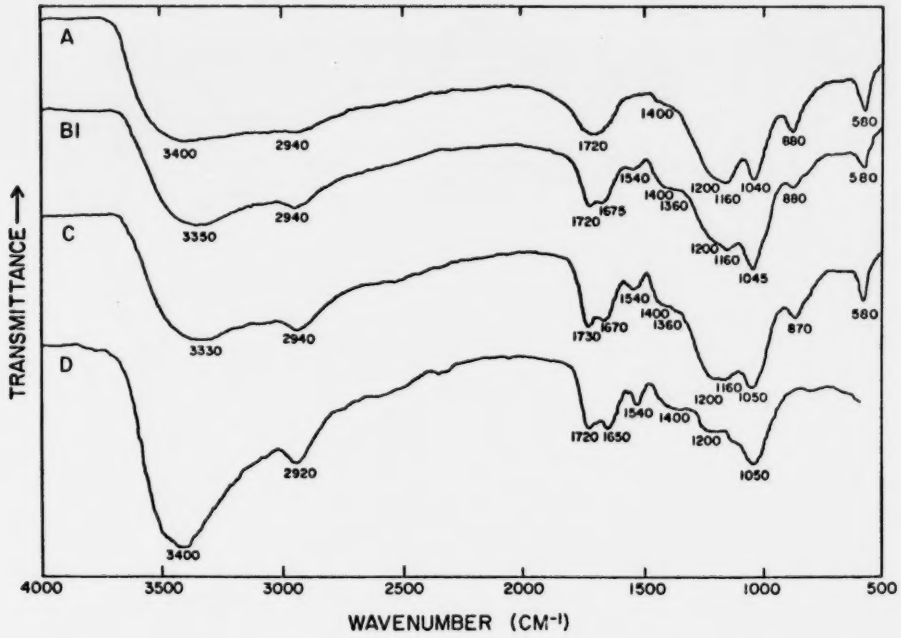

Fig. 3. The infrared spectra of SS fulvic acids A, Bl, and C. The spectrum of fulvic acid extracted from Rifle peat (type III spectrum) is labeled D (Stevenson and Goh, 1971, Fig. 5).

TABLE 35. INTERPRETATION OF THE INFRARED SPECTRA OF SS FULVIC ACIDS

Fulvic acid			
A	B1	C	Interpretation
3400*	3350	3330	Hydrogen bonded OH, NH stretch
2940	2940	2940	Aliphatic CH stretch
1720	1720	1730	C=O in carboxyl group
	1675	1670	C=O (Amide I)
	1540	1540	NH_2 deformation (Amide II)
1400(sh)	1400(sh)	1400(sh)	OH deformation, C-O stretch in phenolic OH groups; CH deformation
1360(sh)	1360(sh)	1360(sh)	S=O in sulfonyl group
1200(sh)	1200(sh)	1200(sh)	C-O stretch and OH deformation in carboxyl group
1160	1160	1160	S=O in sulfonyl group
1040	1045	1050	C-O in polysaccharide
880	880	880	Hydrogen bonded OH deformation in carboxyl group
580	580	580	COOH rock and SO_2 deformation

* Band positions in cm^{-1}.

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portion to their N contents (3.1 and 3.7%, respectively).

The pronounced absorption at 1160 cm^{-1}, the broad band between 1160 cm^{-1} and 1200 cm^{-1}, and the shoulder absorption at 1360 cm^{-1} in the SS fulvic acids can be attributed primarily to the higher sulfur content of these materials. The characteristic absorption bands of the sulfonyl group, SO_2, are commonly found in the ranges 1110-1170 cm^{-1} and 1290-1370 cm^{-1} (Bellamy, 1975; Williams and Fleming, 1973). This fact and the observation that the 1160 cm^{-1} peak appears to increase in absorbance in the order fulvic acid B1 (4.5% S) < fulvic acid C (8.8% S) < fulvic acid A (11.6% S) lend strong support to the connection between absorption near 1200 cm^{-1} and the sulfonyl functional group. It should be pointed out, however, that C-S, C-O, and P-O bonds also contribute in this region (Williams and Fleming, 1973).

The sharp bands at 580 cm^{-1} and 880 cm^{-1} in the SS fulvic acids do not appear in the Type III spectrum and evidently have not been observed in any infrared spectrum of an unfractionated SOM fulvic acid (Stevenson and Butler, 1969; Stevenson and Goh, 1971; Schnitzer and Khan, 1972). However, bands in the region between 550 and 900 cm^{-1} were found by Schnitzer and Skinner (1968) in a low molecular weight fraction of a SOM fulvic acid and were regarded by them as "due to different types of aromatic substitutions." The band at 580 cm^{-1} is in the right place to be interpreted either as a rocking mode of a carboxyl group attached to a benzene ring (Bentley et al., 1968, p. 69) or as a deformation mode of the sulfonyl group (Bellamy, 1975, p. 405). If both of these modes in fact contribute, then the adsorption at 580 cm^{-1} attests to the aromatic character and to the high sulfur content of the SS fulvic acids. It may be noted that the depth of this absorption seems to increase with that of the absorption at 1160 cm^{-1}. Accordingly, the sulfonyl group may be the more important contributor. On the other hand, the band at 880 cm^{-1} may be assigned definitely to the carboxyl group, in particular, to the deformation of a H-bonded OH (Bellamy, 1975, p. 196f; Varsanyi, 1969, p. 368f). This absorption is characteristic of the carboxylic acids and is one of the five principal bands employed in the identification of those compounds (Bellamy, 1975; Tiwari and Sharma, 1970). Since the band does arise from a deformation mode, it is expected to undergo a drastic change if the H bond in which the OH group participates is disrupted. In the absence of H bonding (e.g., in dilute solution), the band disappears (Bellamy, 1975, p. 197). This fact suggests a means for checking the assignment in the case of the SS fulvic acids: The spectrum of a metal-fulvic acid complex should not show the 880 cm^{-1} band, assuming, as is supposed generally (Schnitzer and Khan, 1972), that the OH group must ionize when the carboxyl binds a metal cation. This effect appears in Fig. 4, which is a portion of the infrared spectrum of a low molecular weight fraction of a metal-fulvic acid A complex. In Fig. 4 it is seen that the band at 1720 cm^{-1} in the spectrum of fulvic acid A has disappeared and been replaced by bands at 1580 and 1395 cm^{-1}. These two bands confirm the presence of the carboxylate ion (Williams and Fleming, 1973) and are observed consistently in the spectra of metal-SOM fulvic acid complexes (Schnitzer and Khan, 1972). Therefore, the spectrum reproduced

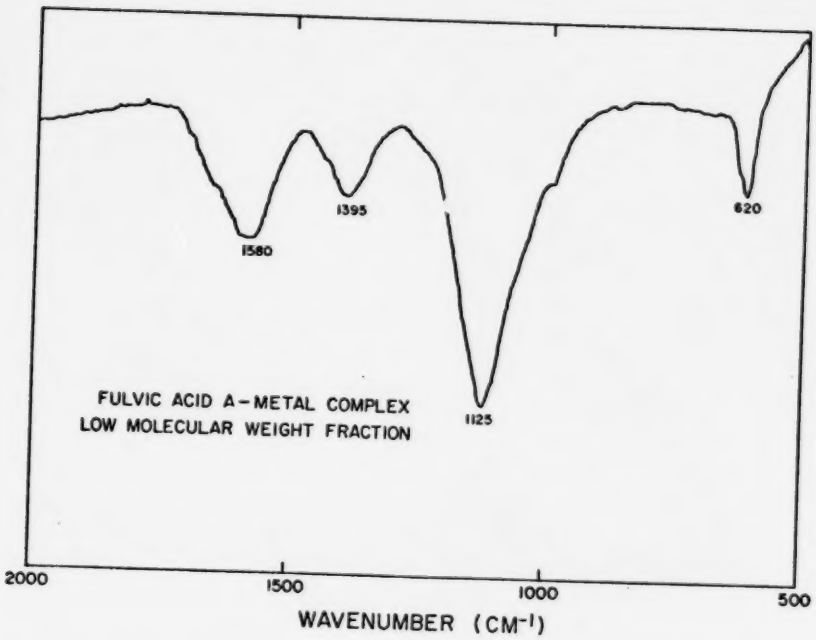

Fig. 4. The fingerprint infrared spectrum of a low molecular weight fraction of a metal-fulvic acid A complex.

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in Fig. 4 rightly may be attributed to a metal-SS fulvic acid complex. Other evidence for this conclusion will be presented later in this section. As expected, the band at 880 cm^{-1} is gone. It is to be noted, however, that the band at 580 cm^{-1} has shifted slightly upward. This behavior is consistent with either vibrational mode (COOH rock or SO_2 deformation) assigned to the band. At present it appears that the 880 cm^{-1} absorption is characteristic of SS fulvic acid, whether pure or complexed with metal.

Infrared spectra of fulvic acids extracted from sewage effluent (SE fulvic acids) have been published by Tan et al. (1971) and by Manka et al. (1974). These spectra are only qualitatively similar to the spectra in Fig. 3, although they do indicate aromatic character and the presence of carboxyl and amide groups. Actually, the spectra of SE fulvic acids seem to be more like the Type II spectrum that is characteristic of low molecular weight fractions of SOM fulvic acids (Stevenson and Goh, 1971). The Type II spectrum displays a very strong absorption at 1720 cm^{-1} indicative of the presence of many carboxyl groups.

Anionic surfactant compounds

It has long been appreciated that anionic surfactants are compounds of environmental concern that may be present in significant quantities in sewage effluents and sludges (Swisher, 1970; Linfield, 1976). The possibility of large-scale application of effluents and sludges on agricultural land has created renewed interest in the chemistry of soil-anionic surfactant interactions, including adsorption phenomena (Clementz and Robbins, 1976; Acher and Yaron, 1977) and the chemical aspects of microbial degradation (Leidner et al., 1976). In the particular case of anaerobically-digested sewage sludges, there is reason to suppose that an appreciable percentage of the dry mass of these materials is attributable to unaltered anionic surfactants, which show a greatly retarded biodegradation under anaerobic conditions (Pitter, 1964; Maurer et al., 1965; Swisher, 1970; Linfield, 1976).

The high S content in SS fulvic acid has been connected with the presence of sulfonyl groups by IR spectroscopy (Sposito et al., 1976) and with SO_3H groups by potentiometric titration studies (Sposito and Holtzclaw, 1977). This relationship, in turn, suggests that sludge-derived fulvic acid may contain the S-bearing anionic surfactants and/or their breakdown products (e.g., the linear alkyl benzene sulfonates and the products of their oxidation reactions).

A rapid analytical procedure was developed for the quantitative determination of unbiodegraded anionic surfactants in the fulvic acid fraction of sewage sludge. This procedure, which is a modification of the methyl green method of Moore and Kolbeson, consists of: (i) hydrolysis in 4N HCl, (ii) separation on an anion exchange resin, (iii) extraction of a methyl green-surfactant complex into benzene, and (iv) colorimetric

determination of the complex. The modified procedure is free of the negative interferences that occurred when the original methyl green method was applied to a sludge-derived fulvic acid and does not require specialized reagents or expensive instrumentation.

An application of the modified procedure to two representative fulvic acids extracted from anaerobically-digested sewage sludges indicated that about 5% of the dry mass of a sludge-derived fulvic acid (water- and ash-free basis) may be attributed to unaltered anionic surfactant compounds. This result suggests that a significant aspect of the chemistry of agricultural soils into which sewage sludge has been incorporated will be reactions involving both unaltered and partially biodegraded anionic surfactants.

The results of applying the method of Moore and Kolbeson (1956) unmodified to fulvic acids A and B1 are given in Table 36. These results suggested that biodegradation of the surfactants normally mixed in with the sludges had occurred extensively. However, when the results were tested indirectly, through the addition of 40 μg Na dodecyl benzene sulfonate (DDBS) to the fulvic acid samples and subsequent analysis by the methyl green procedure, it was found (see column 6 of Table 36) that only about two-thirds of the added surfactant could be recovered. It was concluded from this test that the added anionic surfactant formed relatively strong complexes with other constituents in the fulvic acid samples and, therefore, that the results in column 2 of Table 36 were quite probably inaccurate and low.

TABLE 36. APPARENT ANIONIC SURFACTANT CONTENT AND RECOVERY OF ADDED NA DODECYL BENZENE SULFONATE IN 5-MG SAMPLES OF TWO SLUDGE-DERIVED FULVIC ACIDS (UNMODIFIED METHYL GREEN PROCEDURE).

Fulvic acid	Apparent content of surfactants*	DDBS added	Total surfactant found	Added DDBS recovered	
	μg				%
A	19.23±0.76†	40.0	44.07±0.74	24.84±0.76	62.3
B1	4.53±0.22	40.0	32.10±0.27	27.57±0.27	69.6

* Prior to addition of DDBS.

† All means and mean deviations refer to three replications.

A number of different types of anion exchange resin was utilized during this study in order to find one that best met the criteria of quantitative adsorption and desorption of anionic surfactants in fulvic acid. Certain resins were found to be quite effective in adsorbing surfactant, but would not desorb surfactant well during elution with any of the usual organic solvents. A weakly-basic, analytical grade resin, such as the Bio-Rad AG 3 x 4A, was the only type that provided for an essentially complete recovery of surfactant through an adsorption-desorption cycle. The alkaline methanol-benzene solution proved to be the most effective eluting agent. The addition of KOH to the methanol-benzene mixture was necessary to insure complete desorption of the surfactant compounds from the anion exchange resin. The concentration of KOH employed was that established by Sallee et al. (1956) to be effective in the removal of surfactants from charcoal. The use of more concentrated KOH in an attempt to decrease the volume of eluant required in the present method would have only necessitated the addition of larger volumes of HCl for adjustment to pH 2.5 later on.

The properties of methyl green that recommend it as the most effective dye with which to complex and detect anionic surfactants have been described in detail by Moore and Kolbeson (1956). Most important among these properties are those of relative freedom from interferences, insolubility in the extracting solvent (benzene), and rapid color development. It was found necessary to maintain the H_2O/methanol ratio in the extracting solution at least as large as 4:1 to obtain a linear standard curve. Evidently, the added water insures that the methyl green-surfactant complexes will move quantitatively into the nonpolar benzene layer in the separatory funnel. Although the color development of the methyl green-surfactant complexes was rapid, color stability was not maintained unless the solution containing the complexes remained in a vessel closed to the atmosphere. Otherwise, the complex color intensity decreased significantly after 0.5 hours because of oxidation processes.

As noted by Moore and Kolbeson (1956), several extractions with benzene were necessary to obtain complete recovery of the dye complex. The nature of the reaction between methyl green and surfactant compounds has not been fully elucidated, but it may be supposed that an equilibrium occurs between the dye complex and the uncomplexed surfactant in fulvic acid, such that removal of the complex into benzene sets the stage for additional dye complex formation in the aqueous methanol solution. This newly-formed dye complex comes into a new equilibrium with the remaining uncomplexed surfactant and can be extracted with a further addition of benzene, and so forth.

The results of employing the analytical procedure described in the previous section on fulvic acids A and B1 are given in Table 37 and are summarized as percentages in the last column of Table 38. The data listed in Table 37 show, by comparison with Table 36, that the modified procedure is far superior to the method of Moore and Kolbeson (1956), both in the determination of the quantities of anionic surfactants present in fulvic acid and in the complete recovery of pure DDBS added to fulvic acid. The percentages of unaltered anionic surfactants given in

TABLE 37. ANIONIC SURFACTANT CONTENT AND RECOVERY OF ADDED NA DODECYL BENZENE SULFONATE IN 5-MG SAMPLES* OF TWO SLUDGE-DERIVED FULVIC ACIDS (MODIFIED METHYL GREEN PROCEDURE).

Fulvic acid	Content of surfactant	DDBS added	Total surfactant found	Added DDBS recovered
	μg			%
A	246 ± 9 †	40.0	286.2 ± 0.8	40 ± 1	100
B1	155 ± 1	100.0	254 ± 1	99 ± 1	99

*Sample weight uncorrected for ash and moisture content.

†All means and mean deviations refer to three replications.

TABLE 38. ELEMENTAL AND ANIONIC SURFACTANT CONTENTS OF TWO REPRESENTATIVE FULVIC ACIDS EXTRACTED FROM SEWAGE SLUDGE.

Fulvic acid	%C*	%H*	%N*	%O†	%S*	% Anionic surfactant‡
A	30.3±1.7§	5.20±0.16	1.77±0.18	51.1	11.56±0.95	6.31±0.24
B1	45.2±3.0	7.31±0.28	3.06±0.06	40.0	4.46±0.65	4.29±0.03

*Percentage, water- and ash-free basis, from Sposito et al. (1976)

†Calculated by difference: %O = 100 - % (C + H + N + S).

‡Percentage, water- and ash-free basis.

§Mean deviation computed on data for three different samples of fulvic acid.

Table 38 are in the same relative order as the contents of S in the two fulvic acids, as expected, although the ratio of anionic surfactant percentages is considerably different from the ratio of S percentages.

It is worthwhile to emphasize that the analytical method developed in the present work does not appear to permit the determination of partially biodegraded anionic surfactant compounds, since they are not methylene blue active substances (Leidner et al., 1976). It is quite possible that partially degraded surfactants are important components of anaerobically digested sludges and their fulvic acid fractions. Leidner et al. (1976) have shown recently that LAS transforms rapidly under the action of soil microorganisms to a set of compounds having the same general chemical structure as LAS, but with COOH groups on the ends of the alkyl chains. These compounds are very resistant to further microbial degradation and, therefore, could be abundant constituents of sludge-derived fulvic acid that are not detected by the method described in this report.

Carboxyl group analysis

A rapid and convenient method for the determination of carboxyl groups in soil organic matter, based on techniques developed originally for coal and related materials by Blom et al (1957), was introduced a number of years ago by Schnitzer and Gupta (1965). The method of Schnitzer and Gupta (1965), which will be referred to henceforth as the standard $Ca(OAc)_2$ method, consists of reacting the organic matter to be analyzed for 24 hours with 1N $Ca(CH_3CO_2)_2$, then titrating the resultant mixture potentiometrically with 0.1N NaOH to pH 9.8. The meq COOH groups per gram of sample is calculated straightforwardly using the values of the volume of NaOH required (corrected by a blank titration), the normality of NaOH, and the water- and ash-free mass of the sample.

The method of Schnitzer and Gupta (1965) has enjoyed widespread use in soil organic matter chemistry because of its simplicity and demonstrated accuracy. These positive attributes suggested that the method also might be useful for determining COOH groups in fulvic acid extracted from sewage sludges. However, as with any analytical procedure being adapted to a heterogeneous material, it seemed necessary to consider first the possible interferences that could occur in the method, given the known properties of sludge-derived fulvic acid.

There are two principal ways in which interferences may enter into the standard $Ca(OAc)_2$ method: (i) an interference in the reaction with calcium acetate and (ii) an interference in the titration with NaOH. In the case of sludge-derived fulvic acid, both types of interference are possible because this material contains four different classes of acidic functional groups and is a mixture of organic acids that are associated through hydrogen bonds (Sposito and Holtzclaw, 1977; Sposito et al., 1977). In order for the standard $Ca(OAc)_2$ method to be accurate, the calcium acetate must react only with COOH groups to form the acetic acid that is

titrated subsequently with NaOH. Since sludge-derived fulvic acid possesses sulfonic acid (SO_3H) groups, and possibly other functional groups, that are as strongly acidic or even more strongly acidic than its COOH groups (Sposito and Holtzclaw, 1977), one cannot rule out the interfering reaction of these functional groups with calcium acetate. If these additional groups do react, of course, the meq COOH groups determined by the standard $Ca(OAc)_2$ method will be erroneously high.

Yet another kind of interference can occur with the functional groups in sludge-derived fulvic acid that are significantly less acidic than carboxyl groups. Although these functional groups would not be expected to react with calcium acetate, they can be included in the analysis for COOH groups if they are titratable with NaOH at pH values below 9.8, the pre-determined endpoint pH in the standard $Ca(OAc)_2$ method. This type of positive interference, in fact, already seems to have occurred in some of the test analyses reported by Schnitzer and Gupta (1965). They included four hydroxybenzoic acids in their group of reference compounds for comparing the results of decarboxylation with those of the standard $Ca(OAc)_2$ method. One of these acids (2-hydroxybenzoic acid) possessed a single OH group that was not acidic, while the other three acids possessed at least one acidic OH group in addition to a COOH group. The standard $Ca(OAc)_2$ method compared exactly with the results of decarboxylation for 2-hydroxybenzoic acid, whereas for the other three acids it gave results that were consistently high. This fact suggests that acidic OH groups indeed can be included in the titration step of the standard $Ca(OAc)_2$ method.

Two other sources of interference in the standard $Ca(OAc)_2$ method should be mentioned. Generally the preparation of fulvic acid involves the replacement of inorganic impurity cations with protons through exchange as well as the introduction of residual strong acid during the separation of the fulvic and humic acid fractions (see, e.g., Schnitzer and Khan, 1972, Chap. 2). The subsequent lyophilization of the fulvic acid usually does not remove this residual inorganic acid completely. Therefore, it is possible that calcium acetate mixed with lyophilized fulvic acid in aqueous solution could react with strong inorganic acid to produce acetic acid in addition to that coming from the reaction with COOH groups. This would lead to an overestimation of the meq COOH. Lastly it can be pointed out that a negative interference in the standard $Ca(OAc)_2$ method is possible if the COOH groups are sterically hindered in some fashion from reacting with calcium acetate. This effect could occur in a complex, heterogeneous system, such as fulvic acid, where the molecular configurations are expected to be very irregular.

A detailed experimental examination of the titration behavior and reaction with calcium acetate of a series of model organic acids did, in fact, lead to the conclusion that the standard $Ca(OAc)_2$ method for the determination of COOH groups in organic matter would be ineffective for sludge-derived fulvic acid. In particular, it was shown that positive interferences from SO_3H groups and acidic OH groups could be expected. A modified $Ca(OAc)_2$ method in which these positive interferences do not occur was developed. The method consists of: (i) conversion of fulvic

acid to K/H fulvate, (ii) reaction with 1N calcium acetate, (iii) distillation of the acetic acid product, and (iv) titration of the acetic acid with 0.1N NaOH. The modified method was applied successfully to two representative sludge-derived fulvic acids, a soil-derived fulvic acid, and two model humic polymers, all of which exhibited positive interferences with the standard $Ca(OAc)_2$ method.

Table 39 lists the results of applying the modified method to several humic compounds of current interest. The first two rows in the table give data for samples of sludge-derived FA. It may be seen that the standard $Ca(OAc)_2$ method gave very high values for the apparent meq COOH. These high values caused by the presence of SO_3H groups, acidic OH groups, and residual inorganic acid, are much greater than the typical total meq of titratable functional groups in the two FA samples determined potentiometrically (Sposito et al., 1977). The modified $Ca(OAc)_2$ method, on the other hand, yielded less than 0.75 meq COOH/g for both FA samples. The value of 0.74 $\pm$ 0.03 meq/g found for fulvic acid B1 may be compared with the 0.63 $\pm$ 0.03 meq/g found for the Class II functional groups in another sample of freshly-prepared fulvic acid B1 by Sposito et al. (1977, Table II.2, Exp. 13 and 14). The Class II functional groups* are believed to be primarily COOH groups (Sposito and Holtzclaw, 1977) and the present results tend to confirm this idea. The data in the third row of Table 39 show that the sample of Altamont FA contained residual inorganic acid and interfering acidic OH groups, as well as a COOH content that is about six times that in sludge-derived FA. This value of 4.6 $\pm$ 0.7 meq COOH/g agrees with the value found by Gamble (1972) for the quantity of carboxyls in a soil-derived FA through potentiometric titration. The fact that the meq COOH/g for soil-derived FA is so much larger than for sludge-derived FA supports the results of recent ^{13}C-NMR studies (Sposito et al., 1978b) in which it was observed that the resonances for carbonyls in sludge-derived FA are much less pronounced than in soil-derived FA.

The data in the last two rows of Table 39 are interesting in that they show dramatically the positive interference in the standard $Ca(OAc)_2$ method caused by acidic OH groups. There are no COOH groups in the model humic polymer made solely from hydroxyphenols and hydroxytoluenes (Martin et al., 1972). Nonetheless, the standard $Ca(OAc)_2$ method yields 5.05 $\pm$ 0.05 meq/g because of the presence of the acidic OH groups. The modified $Ca(OAc)_2$ method, on the other hand, yielded the correct value of 0.0 meq COOH/g within experimental error. The model humic polymer made in part from hydroxybenzoic acids is expected to contain both acidic OH and COOH groups and the latter were duly found by application of the modified $Ca(OAc)_2$ method.

---

*Class I, II, III, and IV functional groups are those that are titrated, respectively, at pH < 3, 3-5, 5-8, and > 8.

TABLE 39. CARBOXYL GROUP DETERMINATION USING THE STANDARD $CA(OAc)_2$ METHOD AND THE MODIFIED $CA(OAc)_2$ METHOD.*

Organic Material	Standard $Ca(OAc)_2$ method	Modified method without distillation	Modified method with distillation
	---------- meq/g organic matter ----------		
Fulvic acid A	9.62 ± 0.04	2.83 ± 0.05	0.614 ± 0.022
Fulvic acid B1	9.31 ± 0.10	1.238 ± 0.007	0.740 ± 0.034
Altamont FA	12.52 ± 0.22	9.50 ± 0.34	4.57 ± 0.67
Model humic polymer (Phenolic)	5.05 ± 0.05	5.05 ± 0.05†	0.05 ± 0.05
Model humic polymer (Phenolic and carboxylic)	3.15 ± 0.06	3.15 ± 0.06†	1.19 ± 0.03

*Three replicates, water- and ash-free basis.

†The model humic polymers were not converted to the K form because they do not contain SO_3H groups or residual inorganic acid.

NMR analyses

The FA fraction of sewage sludge has only recently been the object of detailed investigation. Since this organic material is quite heterogeneous, physical methods, such as IR and NMR spectroscopy, may prove to be more useful in its initial characterization than wet-chemical techniques. Infrared spectroscopy has been shown to be effective in elucidating the functional group character of sewage effluent and sludge, especially in relation to the known functional groups in soil-derived FA. Carbon-13 and proton NMR spectra of FA extracted from soil and from seawater have been published very recently by Stuermer and Payne (1976). These investigators found that ^{13}C-NMR spectroscopy is an effective tool for establishing the gross chemical structure of FA and for comparing FA samples of different origin.

Carbon-13 and proton NMR spectra were obtained for two representative fulvic acid samples that were extracted from anaerobically digested sewage sludges. The spectra gave evidence for significant amounts of

both aliphatic and aromatic constituents, including products from the degradation of polysaccharides and proteins. The results suggested that sludge-derived fulvic acid is in a less oxidized state than fulvic acid extracted from naturally occurring soil organic matter. Carbon-13 NMR spectroscopy appears to be a useful means of characterizing fulvic acids and distinguishing these complex, water-soluble mixtures according to the origin and state of oxidation of the organic matter from which they are extracted.

Before embarking on a discussion of the ^{13}C and ^{1}H NMR spectra of the sludge-derived fulvic acids, it is useful to have as a point of reference a summary of the known chemical properties of these organic acid mixtures. Table 40 gives the elemental composition of fulvic acids extracted from sludges A and B1 along with that of the FA samples extracted from soil and from seawater by Stuermer and Payne (1976). Note that all four FA samples have the characteristic properties of relatively low N content (1-6%), relatively high O content, and %C $\leq$ 50. The H/C ratios given in Table 40 suggest that sludge-derived FA will have a fewer number of sites of unsaturation and a greater content of polyhydroxyl compounds than either soil or seawater FA, while the C/N ratios suggest that both sludge and seawater FA will be much richer in protein decomposition products than soil FA. The sludge-derived FA samples have the additional distinguishing property of a large S content. Sulfur was not determined in the soil and seawater FA samples studied by Stuermer and Payne (1976), but its content in them may be expected to range between 0.1 and 2.0%. Infrared spectral and direct quantitative analysis of the sludge-derived FA samples shows that SO_3H groups are present. These functional groups, whose existence is confirmed in potentiometric titration studies, may account for a significant portion of the total S. The ultimate source of these functional groups probably is the organic sulfonate compounds that are found in anionic surfactants. Thus, these groups would not be expected to occur in significant quantities in FA extracted from naturally occurring organic matter. Insofar as other

TABLE 40. ELEMENTAL COMPOSITION OF FULVIC ACIDS EXTRACTED FROM SEWAGE SLUDGE, SOIL ORGANIC MATTER, AND SEAWATER (WATER AND ASH-FREE BASIS).

FA sample	% C	% H	H/C	% N	C/N	% S	% O
Ontario sludge (A)	30.	5.2	2.1	1.8	19.2	12.	51.
Rialto sludge (B1)	45.	7.3	1.9	3.1	17.0	4.5	40.
Podzol soil	47.	4.5	1.1	0.5	110.	ND	48.
Sargasso Sea	50.	6.8	1.6	6.4	9.0	ND	37.

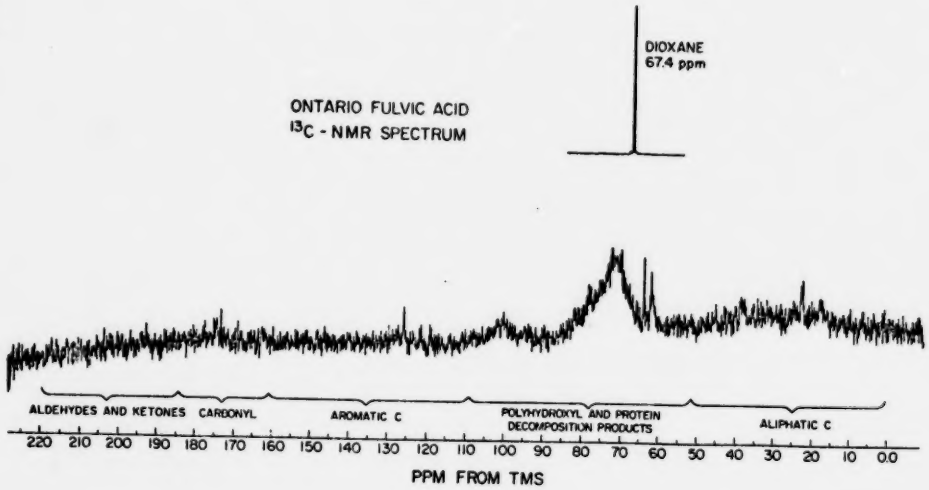

Fig. 5. 22.638 MH_z ^{13}C-NMR spectrum of Ontario FA. Result of 37 900 scans using 90° pulse and total pulse delay and acquisition time of 1.36s

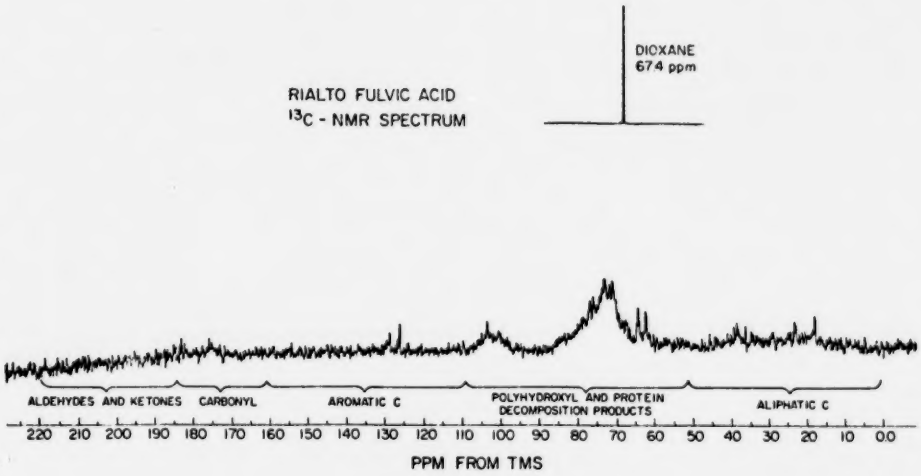

Fig. 6. 22.638 MH_z ^{13}C-NMR spectrum of Rialto FA. Result of 45 444 scans using 90° pulse and total pulse delay and acquisition time of 1.36s

acidic functional groups are concerned, however, Ontario (A) and Rialto (B1) FA are similar to other fulvic acids in comprising COOH groups, phenolic OH, and N-containing functional groups.

The ^{13}C-NMR spectra of Ontario and Rialto FA are presented in Figs. 5 and 6, respectively. These spectra, which are quite similar despite differences in the chemical composition of the two fulvic acids, show the complex absorption patterns and broad resonances that are expected for complicated molecular systems, but their resolution is better than that in any ^{13}C spectrum of fulvic acid reported previously. The interpretation of the spectra is given in the following paragraphs and is based on standard references. A lengthy discussion of the problems of interpretation for mixtures of macromolecules has been given by Stuermer and Payne (1976).

The resonances between 10 and 60 ppm are characteristic of aliphatic carbon atoms. These are fairly prominent in the two sewage sludge FA samples, more so than what is observed for soil FA. This fact may reflect the input of both animal and industrial wastes into sewage sludge; soil organic matter which derives from the decomposition of plants usually has only a small percentage of aliphatic compounds in its FA fraction.

Resonances in the range 50-110 ppm generally represent carbon atoms in polyhydroxyl compounds as well as those in certain amino acids. These resonances are the most pronounced in the ^{13}C spectra of the two sludge FA samples. The particularly sharp resonances in the range 60-65 ppm may correspond, e.g., to CH_2OH in polysaccarides or, possibly, to amino acids and other protein decomposition products. The broad resonances at 72 and 101 ppm likely are due to polysaccharides in some phase of degradation. Fulvic acid extracted from soil does not exhibit resonances as prominent as those in Figs. 5 and 6 in the polyhydroxyl range. In fact, the resonances are no more pronounced than those for aliphatic constituents. This difference between the sludge and soil FA spectra probably stems from the anaerobic conditions under which the sludges were produced. Under anaerobic conditions, the decomposition of polysaccharides and proteins should be arrested somewhat. It is worthwhile to note in passing that the IR spectra of Ontario and Rialto FA show deep absorptions near 1045 cm^{-1} that may be assigned to C--O in polysaccharides.

The resonances in the range 110-160 ppm indicate aromatic, heteroaromatic, and olefinic compounds. These resonances show prominently around 125 ppm, which suggests the significant presence of substituted benzene rings. The same conclusion applies to soil FA.

The resonances between 160 and 185 ppm may be assigned to carbon atoms in carboxyl and in amide groups. These resonances are not particularly strong in the ^{13}C spectra of the two sludge FA samples, in contrast with the spectrum of soil FA, where, for example, the carbonyl C resonance is the most prominent feature. This result is in accordance with the IR spectra of sludge and soil FA samples, which show that sludge FA tends to exhibit a relatively weaker absorption than soil FA at 1720

cm^{-1}, indicative of C==O in COOH. The difference in the spectra once again may be explained on the basis of the anaerobic conditions that produced the sludge samples and that would inhibit oxidation and COOH production. The same explanation would apply to the weak resonance near 193 ppm, characteristic of C==O in aldehydes and ketones, that appears in the ^{13}C-NMR spectrum for Ontario FA.

The ^{1}H-NMR spectrum of Rialto FA is presented in Fig. 7. The broad resonances centered at 0.90 and 1.30 ppm indicate protons on aliphatic carbon atoms (CH_3--R and R'--CH_2--R, respectively), while the sharp resonances near 2.0 ppm indicate protons on carbons adjacent to carbonyl groups, to aromatic molecules, and to alkenes. The broad, pronounced resonance near 3.8 ppm may be assigned primarily to protons in polysaccharide decomposition products. This resonance, which is the most prominent feature in the ^{1}H-NMR spectrum of Rialto FA (excepting the H_2O-HDO resonance), corroborates the assignment of the strong resonances at 72 and 101 ppm in the ^{13}C-NMR spectrum. The complicated series of resonances in the range 7.3-8.2 ppm in Fig. 7 indicates that a complex variety of aromatic protons exists in sludge-derived FA.

Carbon-13 NMR spectroscopy appears to be an effective means for investigating the organic structures to be found in complex, heterogeneous mixtures such as FA. It seems quite possible that detailed structural information about sludge-derived FA could be obtained by separating this material into fractions using column chromatography and then studying the fractions with ^{13}C- and ^{1}H-NMR spectroscopy. This possibility currently is under investigation.

It is worthwhile to point out that the differences between sludge and soil fulvic acids shown in their ^{13}C-NMR spectra imply that the water soluble organic compounds in sewage sludges would be microbiologically unstable in the soil environment. Thus, it would be expected that the initial speciation of organic molecules and of trace metals in the soil solution after the addition of sludge may change significantly with time as the compounds more susceptible to microbial attack (e.g., surfactants and polysaccarides) are degraded and the functional group character of the material changes.

Trace metal-fulvic acid mixtures

At present, the chemical mechanisms by which potentially harmful trace metals contained in sewage sludges become soluble species after the incorporation of sludge into soil are only a matter for speculation. It is reasonable to suggest that the organic constituents of sludges will play a signficant role in the speciation of metals such as Cd, Cu, Ni, Pb, and Zn, but the degree to which soluble complexes between these metals and sludge-derived organic compounds actually form in a soil solution will depend on the functional group character and water solubility of the organics, as well as on the number and stability of other possible trace metal compounds and surface phases.

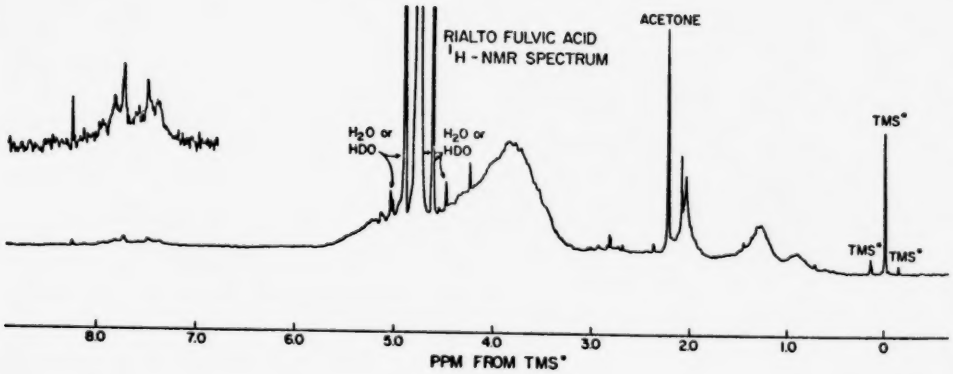

Fig. 7. 90.020 MHz ^{1}H-NMR spectrum of Rialto FA dissolved in D_2O. Result of 6 022 scans using 90° pulse. Resonance marked "acetone" due to solvent impurity in sample tube. Features marked with asterisk are spinning sidebands due to intense H_2O-HDO and TMS* resonances.

The distribution of Al, Cd, Cu, Fe, Ni, and Zn among the organic and inorganic fractions extracted from sewage sludges using 0.5N NaOH has been studied recently by Holtzclaw et al. (1978). Data obtained for four different sludges showed that most of the Al and Fe and much of the Zn extracted were associated with a precipitable, largely inorganic fraction, that most of the Cu and a significant portion of the Zn extracted were associated with the humic acid (HA) fraction, and that most of the Cd and Ni extracted was associated with the FA fraction. These results suggest the need to study, in particular, the complexes that may occur between sludge-derived HA and Cu and Zn, and between sludge-derived FA and Cd and Ni. The possibility of extraction of trace metal-FA complexes from sludge has in fact been demonstrated recently (Sposito et al., 1976). In a preliminary experiment, a trace metal-FA solution was extracted from a sewage sludge by a modification of the method for extracting and purifying FA that was developed by Holtzclaw, et al. (1976). This solution was separated into components by gravity filtration on a column of Sephadex G-10 gel and the eluted fractions were analyzed for C, Cd, Cu, Fe, Ni, Zn, and inorganic salts. The resultant elution diagrams could be interpreted as evidence that Fe, Cu, and possibly Zn had formed complexes with the sludge-derived FA, while Cd and Ni were associated with the inorganic salt fraction (perhaps as Cl complexes). The applicability of this conclusion to other sludges with different chemical composition was not investigated, nor were any studies of the structural chemistry of the eluted complexes undertaken in these initial experiments.

These initial gel filtration studies were followed by experiments in which trace metal-fulvic acid solutions, extracted with NaOH from two chemically different sewage sludges and separated from humic acid using HCl, were fractionated on a column of Sephadex G-10 gel using deionized water at pH 5.65 as the eluant. The effluent from the gel was analyzed in 3-ml increments for organic C, Cl, and the metals Cd, Cu, Fe, Ni, and Zn. Elution diagrams prepared with the analytical data showed multiple maxima in organic C concentration and a single maximum in Cl concentration (indicating the presence of inorganic salts). Fe and Cu showed concentration maxima that followed closely those in both the organic and inorganic fractions, while Cd, Ni, and Zn tended to show maxima following the inorganic fraction peak and only one or two of the organic C maxima. The data indicated that Cu and Fe formed complexes with sludge-derived fulvic acid (FA) under conditions of the experiment. Cd, Ni, and Zn were associated with the FA only weakly, in a manner dependent on the nature of the sludge, and in the relative order of affinity Zn Ni Cd. These data suggested that sludge-derived FA behaves toward trace metals as a relatively harder Lewis base than Cl^-.

Infrared spectra of the eluted organic fractions indicated that protein decomposition products and polysaccharide components appear in the fractions of relatively larger molecular size, as do the components containing SO_3H groups. The IR spectra also gave evidence that COOH and SO_3H functional groups are involved in metal-FA interactions. An important organic fraction of sludge-derived FA was identified that appears to be an aliphatic, carboxylic acid mixture which can complex only Cu significantly.

Elution diagrams, showing the relative concentration of organic C, a particular metal, and Cl as a function of elution volume, are shown in Figs. 8 through 12 for the five metals Fe, Cu, Cd, Zn, and Ni, and for the two FA samples. These data are composites of several elution experiments (although the data shown for a given element were obtained in a single run) in which checks for reproducibility were performed.

In the cases of Fe and Cu (Figs. 8 and 9), it may be seen that the positions of some of the relative maxima in metal concentration are quite close to those of the maxima in C concentration. (The heights of these peaks, of course, have no comparative signficance because of the differences in total concentration between C and metals.) The considerable fluctuation in Cu concentration that appears in the elution diagram for metal-FA solution B1 is in part caused by instrumental resolution problems associated with the very low total Cu concentration. The close correspondence of the peak positions is in agreement with the results of Bender et al. (1970), who studied Cu-spiked sewage effluent by filtration on a column of Sephadex G-25 gel, and may be taken as evidence that Fe- and Cu-FA complexes occur importantly under the conditions of the present experiments. It may be noted that an exact congruence of the metal and organic C concentration maxima is not required to infer the presence of complexes. In a heterogeneous mixture of organic compounds, it may be expected that a given fraction of the mixture that has been separated according to molecular size will not necessarily be homogeneous with respect to its affinity for trace metals. Thus, a maximum in trace metal concentration in an elution diagram may be displaced from that in organic C concentration if the wings of the C peak represent compounds with a greater affinity for the metal in question than does the center of the peak. This effect was in fact observed by Bender et al. (1970) in the case of Cu.

The Cl concentration maxima in Figs. 8 and 9 are close in position to one or more maxima in the concentrations of Fe and Cu. This fact suggests that inorganic forms of Fe and Cu, some of which may be Cl complexes, are also important in the metal-FA solutions. As in the case of the peaks in C concentration, there need not be exact coincidence in the peaks in metal and Cl concentration. If there is an adverse effect of ionic strength on Cl complexation, for example, metal-Cl complexes may form preferentially when the inorganic salt concentration is lower, and the metal concentration peak may be displaced from that for Cl in an elution diagram.

The elution diagrams for Cd, shown in Fig. 10, suggest that this metal may behave differently in different sludge-derived FA. Although both diagrams in Fig. 10 show a close correspondence in the positions of Cd and Cl maxima, indicating a significant concentration of Cd in an inorganic form, there is some tendency for Cd to associate with the most retarded organic fraction in both metal-FA solutions and with the most mobile organic fractions in metal-FA solution B1. (The fluctuations in relative Cd concentration noted in the elution diagram for metal-FA solution B1, as with the Cu data, are in part due to instrumental resolution problems associated with the very low total Cd concentration).

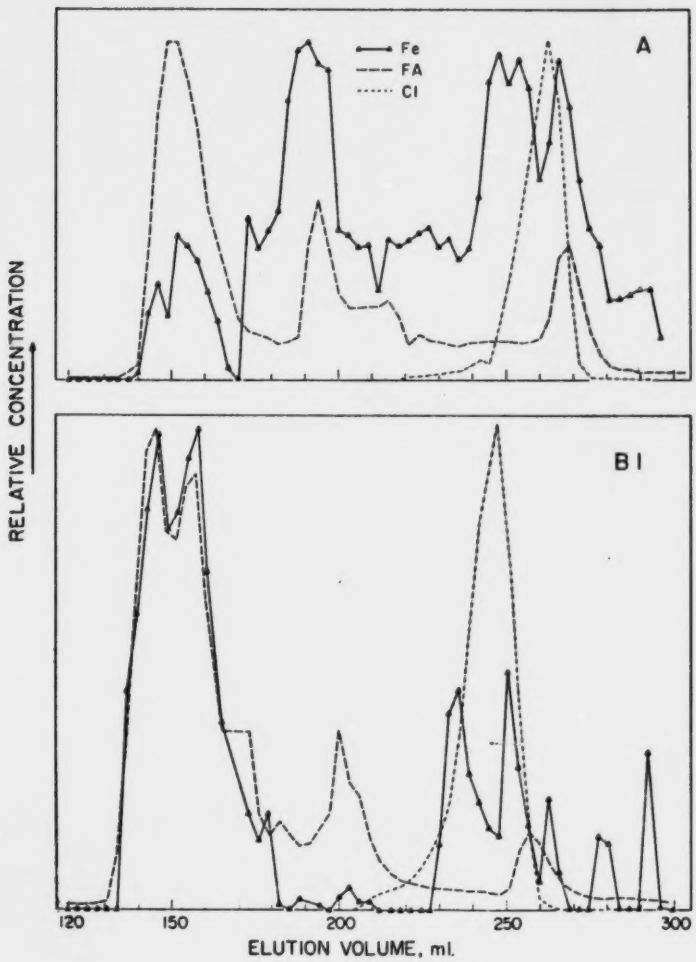

Fig. 8. Elution diagrams for Fe in metal-FA solutions A and Bl.

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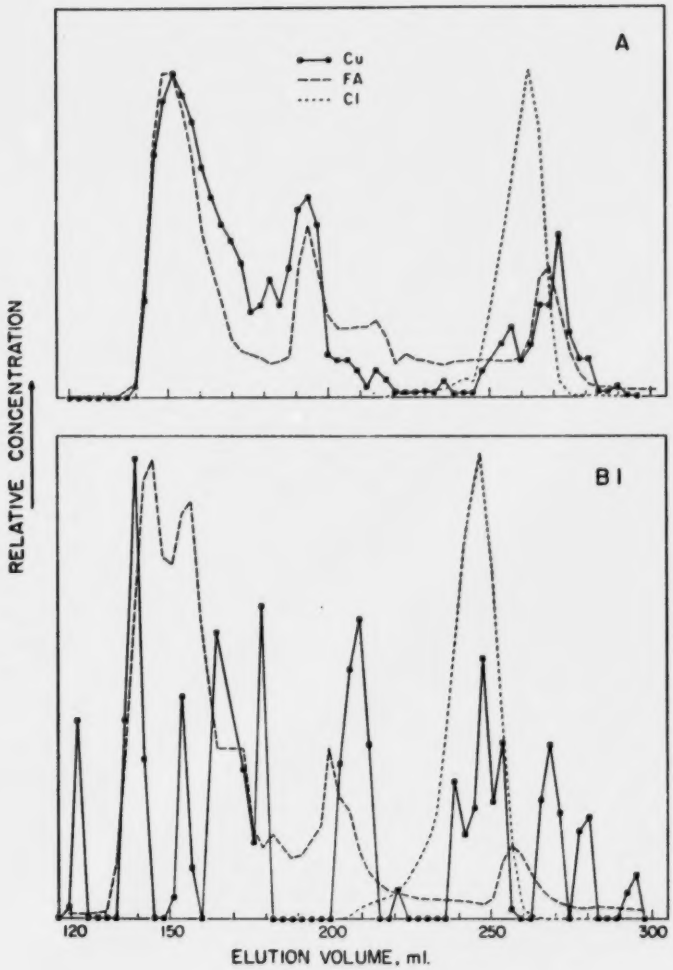

Fig. 9. Elution diagrams for Cu in metal-FA solutions A and Bl.

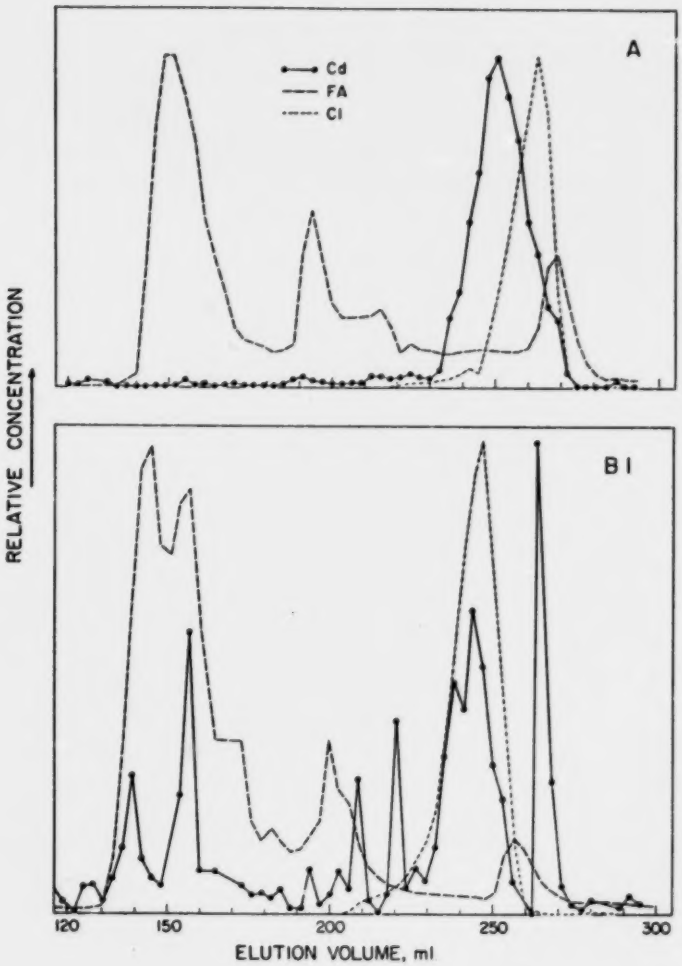

Fig. 10. Elution diagrams for Cd in metal-FA solutions A and B1.

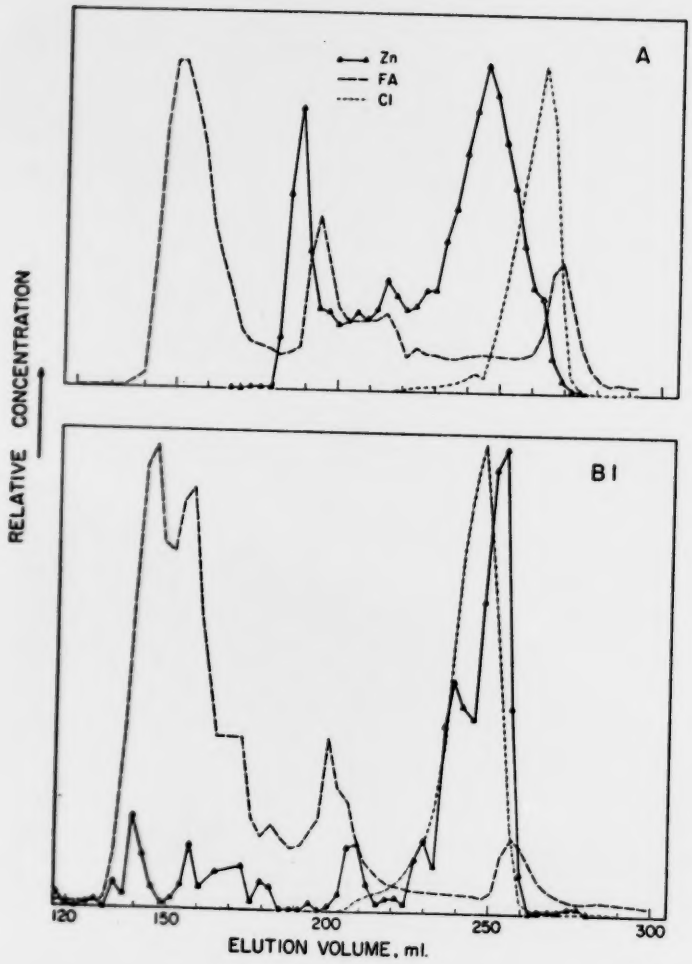

Fig. 11. Elution diagrams for Zn in metal-FA solutions A and B1.

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Since Cd^{2+} is a rather soft Lewis acid and Cl^- is a soft Lewis base, a close association between the Cd and Cl concentration maxima and the formation of Cd-Cl complexes would not be surprising (see, e.g., Huheey, 1972, p. 227; Sposito, 1977; Sullivan, 1977). The differences between the Cd associations with the organic fractions in the two FA solutions may point to a difference in Lewis basicity of the organic functional groups. Indeed, the much larger content of the hard-acid SO_3H groups in fulvic acid A as compared with B1 (Sposito and Holtzclaw, 1977) would suggest that A, when ionized, will behave as a harder Lewis base than B1 and accordingly will have a lesser tendency to complex soft Lewis acids such as Cd^{2+}.

These same conclusions may be applied to the case of Zn, shown in Fig. 11. Zinc tends to be associated with the Cl maximum for both metal-FA solutions, but it also shows a relatively pronounced tendency to follow the organic fractions eluted at intermediate volumes in the case of metal-FA solution A. Given that Cd is a significantly softer Lewis acid than Zn (see, e.g., Sullivan, 1977), a comparison of Fig. 10 and 11 indeed suggests that fulvic acid B1 has a somewhat softer Lewis base character than does fulvic acid A and, therefore, that the stability of Cd complexes with fulvic acid B1 would be greater than with fulvic acid A. Complexes with Zn would show the opposite trend.

The elution diagram for Ni, shown in Fig. 12, indicates that this metal predominately is in an inorganic form in metal-FA solution A. (Reliable data for metal-FA solution B1 unfortunately could not be obtained because of the low total concentration of Ni). There is a small tendency for the metal to follow some of the intermediate organic C maxima, which was not detected in preliminary experiments (Sposito et al., 1976). This result is rather surprising, since Ni ordinarily would be expected to form more stable organic complexes than Zn (Huheey, 1972, p. 229) and, in fact, does so with soil-derived FA (Schnitzer and Khan, 1972, p. 220)

A more complete picture of the association of the five trace metals with the organic and inorganic fractions eluted from the Sephadex G-10 column is given in Table 41, which lists the percentage distribution of the metals among the organic C concentration maxima. Although these data must be regarded as semi-quantitative, a general conclusion may be drawn from them. Iron, for example, is distributed differently among the organic C peaks in metal-FA solution A than it is in metal-FA solution B1. Copper associates preferentially with the first two organic C peaks in metal-FA solution A and with the first, third, and fifth organic C peaks in metal-FA solution B1. These kinds of differences reflect clearly the fact that the complicated, heterogeneous nature of sludge-derived FA makes for a detailed scheme of metal binding that will depend on the exact molecular composition of a given sludge.

Infrared spectra of the six organic fractions of metal-FA solution B1 are reproduced in Fig. 13. The IR spectra of the organic fractions of metal-FA solution A were quite similar to the ones shown here. An analysis of the IR spectrum of unfractionated fulvic acid B1 has been given

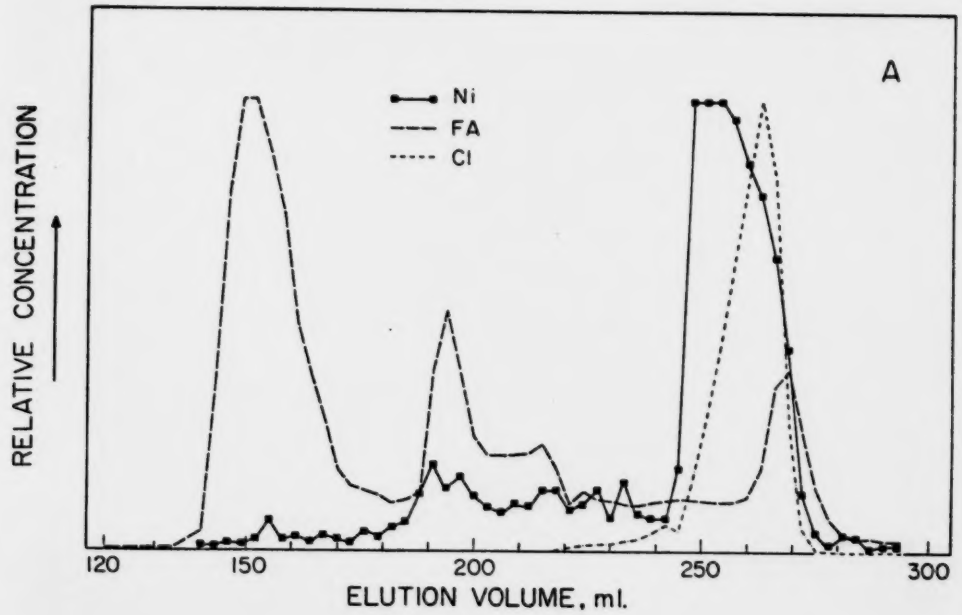

Fig. 12. Elution diagrams for Ni in metal-FA solutions A.

TABLE 41. PERCENTAGE DISTRIBUTION (BY WT) OF FIVE TRACE METALS AMONG THE PRINCIPAL ORGANIC AND INORGANIC FRACTIONS IN TWO METAL-FA SOLUTIONS SEPARATED ON SEPHADEX G-10 GEL

Metal-FA solution	Metal	Organic fraction* 1	2	3	4	5	6	Cl
A	Cd	<1	1	2	6			86
	Cu	59	25	1	12			5
	Fe	9	32	3	17			24
	Ni	1	11	6	15			61
	Zn	<1	22	14	3			58
B1	Cd	8	14	4	1	7	5	32
	Cu	16	6	17	7	17	<1	16
	Fe	29	40	6	2	<1	8	13
	Zn	6	4	5	2	8	47	28

*Designated by peak number, in order of increasing time of retention by the gel column. The metal percentages in each row may not sum to 100 because of experimental error and/or because not all of the content of a given metal is associated only with the maxima in organic C and Cl.

viously (Sposito et al., 1976). This analysis may be used as a basis for interpreting the spectra in Fig. 13, since colloidal inorganic impurities were visually absent from the metal-FA solutions and aqueous inorganic species would appear in the Cl peak. The gradual disappearance of absorptions near 1540 cm^{-1} (NH_2 deformation) and 1040 cm^{-1} (C--O stretch), relative to that near 1640 cm^{-1} (COO^-), for example, in going from organic C peaks 1 to 4, may be correlated with a diminishing content of protein decomposition products and polysaccharides, respectively. This trend is expected, since these two constituents of FA should be of relatively large molecular size and, therefore, should be eluted early from the gel column. Two other prominent features of the IR spectra in Fig. II.12 are the persistence of aliphatic components (absorbing near 2930 cm^{-1} throughout the organic fractions and the presence of carboxylate ions, evidenced by adsorptions in the wave-number ranges 1680-1550 cm^{-1} and 1400-1390 cm^{-1} (Bellamy, 1975). The COO^- absorptions indicate that metal

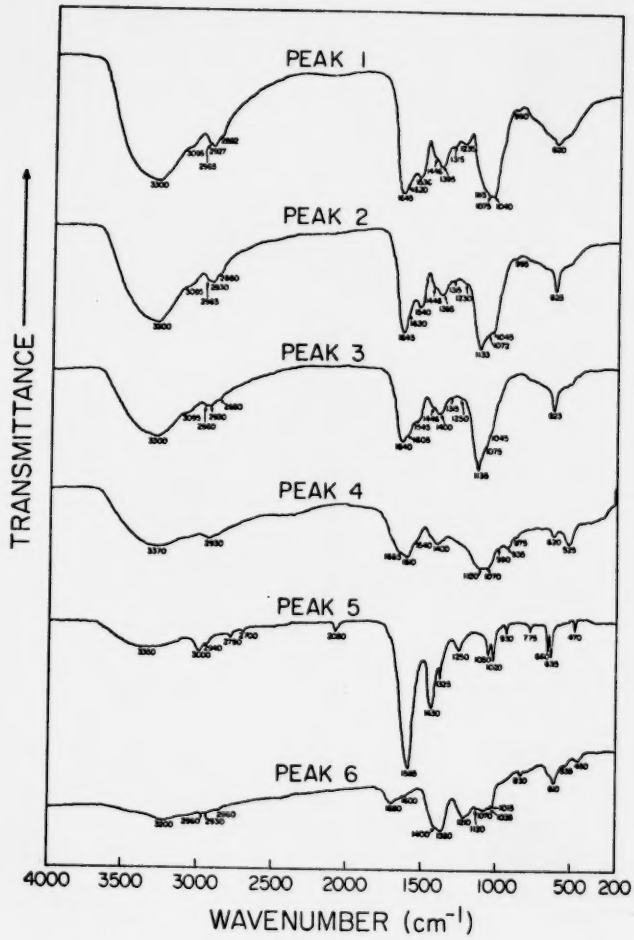

Fig. 13. Infrared spectra of the principal organic fraction in metal-FA solution B1. The spectra are labeled according to peaks associated with increasing elution volume from peak 1 through peak 6.

complexation by carboxyl groups is an important mechanism of metal-FA interaction for sludge-derived FA, just as it is for FA extracted from naturally occurring soil organic matter (Vinkler et al., 1976).

The S in sludge-derived FA is believed to occur significantly in SO_3H groups (Sposito et al., 1976; Sposito and Holtzclaw, 1977). The sulfonate ion absorbs strongly in the wavenumber regions 1240-1120 cm^{-1}, 1080-1025 cm^{-1}, and near 610 cm^{-1} (Baldinus, 1976; Bellamy, 1975); evidently this anion should be present in a metal-FA mixture if metal sulfonates have formed. Pairs of bands in the first two indicated ranges of wavenumbers (near 1120-1130 cm^{-1} and 1070 cm^{-1}, respectively) and near 620 cm^{-1} in fact do appear in the IR spectra of each of the organic fractions in metal-FA solution B1, with the exception of the fraction corresponding to the fifth organic C maximum. The greatest relative absorption is by the organic fractions eluted first from the gel, although the absorption does not diminish as quickly with elution volume as does that due to polysaccharides. From this fact it may be concluded that metal complexation by sulfonic acid groups occurs in sludge-derived FA, and that the sulfonic acid groups are associated principally with components of FA having a relatively large molecular size.

The IR spectrum of the organic fraction corresponding to the fifth organic C maximum in the elution diagram for metal-FA solution B1 has a very different appearance from all of the other spectra in Fig. 13. The absorption due to SO_3^- is absent, that due to OH in the 3000 cm^{-1} region is much less pronounced, and that due to COO^- is much more pronounced than in the other spectra, for example. Also, the absorptions in the fingerprint region are much sharper than what is customarily observed for FA samples, which fact suggests that this organic fraction is relatively homogeneous in composition. The IR spectrum as a whole is quite similar to that of the salt of an aliphatic acid (Meiklejohn et al., 1957; Bellamy, 1975). However, a definite identification awaits further experimentation. It may be noted that this fraction is the one that was not detectable by an absorbance measurement at 465 nm and that it was not associated with an appreciable percentage of Fe, even though it accounts for about 13% of the total amount of organic C in metal-FA solution B1. The lack of absorbance at 465 nm is probably the result of negligible complex formation with Fe.

The IR spectrum of the organic fraction corresponding to the sixth organic C peak in the elution diagram for metal-FA solution B1 suggests a phenolic mixture (strong absorptions at 1400 and near 1200 cm^{-1}) with a contribution from ketones and aldehydes (1690 and 1360 cm^{-1}), as well as SO_3^- functional groups. The relatively nonpolar nature suggested for this fraction is consistent with the fact that it eluted from the G-10 column <u>after</u> the inorganic salts. Determann (1968) and Determann and Lampert (1972) have observed that strong hydrophobic interactions between Sephadex gels and nonpolar aromatic units may occur, leading to the adsorption of these units by the gel. This adsorption is pronounced in an electrolyte solution, but the adsorbed compounds can be eluted with distilled water and generally will move down the column near the electrolyte solution-distilled water interface (Lindqvist, 1967). Thus, it may

be concluded that the most retarded organic fraction in metal-FA solution B1 is an aromatic mixture that is adsorbed reversibly by the G-10 gel and, therefore, is eluted out of the sequence expected on the basis of molecular size.

Gel filtration chromatography of trace metal-FA solutions extracted from two chemically different sewage sludges indicated that Fe and Cu formed organic complexes with almost all of the constituents of the FA fraction under the chemical conditions arising during its extraction and pH adjustment. Under these same conditions, Zn, Ni, and especially Cd showed relatively little tendency to associate with the organic fractions of FA. Based on the data in Figs. 8 to 12 and in Table 41, the relative order of affinity of the organic fractions for the trace metals is: Cu $\geq$ Fe $\geq$ Zn $\geq$ Ni $\geq$ Cd.

It is worthwhile to consider the extent to which the observed affinity series may reflect the presence of the Cl^- ion. This point may be examined with the help of the data presented in Table 42, which gives the speciation of the five metals studied in a solution having the same pH (5.65), Cl^- concentration (1.86×10^{-1} M), and trace metal concentrations as metal-FA solution A. The speciation was calculated using the computer program GEOCHEM. The principal cation was taken to be Na^+, which was included in sufficient concentration to maintain the solution electrically neutral; the computed ionic strength of the solution was 0.19M. Table 42 shows that the order of chloride complexation is Cd $\gg$Cu $\geq$ Ni $\gg$Zn $\gg$Fe. If all of the chloride complexes were the determining factor in the present experiments, one might expect that the organic affinity series would be the reverse of the Cl affinity series.

TABLE 42. CHLORIDE COMPLEXATION IN A SOLUTION HAVING THE SAME pH VALUE AND CONCENTRATIONS OF Cd, Cu, Fe, Ni, Zn, AND Cl AS METAL-FA SOLUTION A.

Metal cation	Cd^{2+}	Cu^{2+}	Fe^{3+}	Ni^{2+}	Zn^{2+}
% MCl	47.86	8.71	0.00	2.19	3.63
% MCl_2	23.44	0.21	0.00	5.13	0.89
% MCl_3	1.15	0.00	0.00	0.17	0.00
% MCl_4	19.05	0.0	0.00	0.00	0.00
% MOHCl	0.00	0.00	0.35	0.00	0.02
% M^{2+}	8.36	90.88	*	92.46	95.46

*99.6% of Fe^{3+} is found as a hydroxy complex, mostly $Fe(OH)_2^+$.

An alternative possibility is that only the neutral or negatively charged Cl complexes should be considered as competing successfully with the organic ligands, since the positively charged Cl complexes conceivably could be bound to organic functional groups. In that case the Cl affinity series is Cd >> Ni >> Zn > Cu > Fe. The reverse of this series is essentially the same as the observed affinity series for organic ligands in FA. Therefore, it may be concluded that, at pH 5.7 and ionic strength = 0.2M, the organic ligands in a FA solution containing approximately 0.2M NaCl would behave toward Cd, Cu, Fe, Ni, and Zn like a Lewis base that is relatively harder than Cl^-. Accordingly, as observed, these ligands would compete well with Cl^- for the relatively hard metal cations (e.g., Fe and Cu) and would not compete well for the relatively soft metal cations (e.g., Cd and Ni).

2.2. TRACE METAL-FULVIC ACID COMPLEXES

Proton complexation

The chemical properties of the acidic functional groups present in fulvic acid extracted from sewage sludge are believed to be of central importance to an understanding of how the chemistry of the soil solution may change after the application of sludge to agricultural land. Sewage sludges generally contain significant amounts of potentially harmful metals (Page, 1974) whose behavior in soil will be influenced strongly by the presence of acidic organic compounds that can form complexes with them. Some of these organic compounds will occur naturally in the soil; their chemical properties have been the subject of intensive investigation for a number of years (Schnitzer and Khan, 1972). Others will come from the sludge itself and their properties must be known in order to predict accurately the fate of the trace metals.

The dissociation of protons from fulvic acid (FA) extracted from sewage sludge was investigated recently by potentiometric titration (Sposito and Holtzclaw, 1977). In that study, a number of important facts were brought to light that suggest that the behavior of this material in soil solutions will be complex. For example, there appear to be four separate classes of dissociable functional groups that range in acidity from very strong (ionized at pH < 2) to very weak (ionized at pH > 10). These classes are just four out of a continuum of classes of functinal group acidity in sludge-derived FA, since no acid or alkaline final endpoints appear in the titration curve between pH 1 and 11. In this report, the functional group classes will be designated I, II, III, or IV as those that titrate approximately in the pH ranges < 3, 3-5, 5-8, or > 8, respectively.

Another important feature of the titration curve for sludge-derived FA is that it may show a pronounced maximum followed by a minimum at pH values very near the endpoint for the class I functional groups, which are believed to be SO_3H groups (Sposito and Holtzclaw, 1977). This

behavior stems from the polyacid nature of FA, which permits weak ion-pair formation with protons in solution as a result of a buildup of a high density of negative charge on the polyanion and consequent changes in molecular conformation (Sposito and Holtzclaw, 1977). Still another complicating aspect of the titration curve for FA extracted from sludge is the fact that the curve is strongly dependent on the concentration of FA in solution. This result means that FA molecules are associated, i.e., that FA is a polynuclear polyacid. The total acidity of sludge-derived FA, as measured by the sum of titratable protons for all of its classes of functional groups, will also depend on its concentration.

It is evident from the discussion just given that the solution chemistry of sludge-derived FA will be rather complicated. On the other hand, the most important characteristics of this material insofar as acidic properties are concerned can be represented in terms of a simple, quantitative model. Granted that the extraction of the fulvic acid fraction from a sludge produces an assembly of organic molecules whose individual properties vary widely, it still appears that the assembly as a whole possesses average properties that are classifiable and describable in terms of a few macroscopic parameters. For example, the acidic functional groups fall into just four classes, each describable in principle by a certain number of equivalents of dissociable protons and a protonation equilibrium constant, although on the molecular level it is probable that no two acidic functional groups are chemically the same. Thus, it may be reasonable to consider FA as an assembly of identical mean fulvic acid units whose chemical properties replicate those of the true, heterogeneous mixture. A mean fulvic acid unit is a hypothetical macromolecule that contains one or more distinct classes of acidic functional groups and is able to associate with other mean fulvic acid units or with part of itself (self-association) through the mechanism of hydrogen bonding. The protonation and association properties of an aqueous solution of mean fulvic acid units were considered in detail by Sposito et al. (1977). There it was shown that the titration curve for FA, in the context of this model, can be described in terms of the expression

$$n_H([H], Fu_T) = \sum_i \frac{n_H^{\,i}\, {}^cK_{HA_i}[H]}{1 + {}^cK_{HA_i}[H]} \qquad (24)$$

where n_H is the number of milliequivalents of protons bound to unit mass of FA and is a function of [H], the hydrogen ion concentration in solution, and of Fu_T, the total FA concentration. The parameter $n_H^{\,i}$ and ${}^cK_{HA_i}$ in Eq. [24] are, respectively, the total number of milliequivalents of protons that can be bound by functional groups in the ith class, and the conditional protonation constant for the ith class of acidic functional groups $n_H^{\,i}$ is in general a function of Fu_T, ionic strength, and temperature. The conditional protonation constants generally will depend on these variables, as well as on [H].

Aqueous solutions of two fulvic acids extracted from sludge-soil mixtures and converted to K-fulvates were titrated potentiometrically at 25°C with HCl in ionic media of 0.1M and 0.2M KCl. Data were obtained for a range of concentrations of FA, although during a titration experiment both FA concentration and ionic strength were rigorously held constant. The simple model described above was employed to interpret the formation functions calculated using the titration data. As mentioned previously, this model ascribes the acidic properties of a FA solution to an assembly of hypothetical macromolecules ("mean fulvic acid units") that contain several distinct classes of functional group and are able to associate through hydrogen bonding. Conditional protonation constants were computed for each class of acidic functional group that protonates in the pH range 3-11. The common logarithms of the average protonation constants at 25°C were found to be 3.9, 6.5, and 9.4 for the three classes of weakly acidic functional groups studied. These values were independent (within experimental error) of FA composition and concentration, and of ionic strength in the range investigated.

The common logarithms of the mean values of the conditional protonation constants, computed using the titration curves for the three principal classes of weakly acidic functional groups in fulvic acids A and B1, are listed in Table 43. Typical titration curves appear in Fig. 14. The lines through the data points are not the results of statistical fits. They represent plots of Eq. [24] using the values of ${}^{c}K_{HA_i}$ and n_H^i (i = II, III, IV) given in Table 43. The data show that log ${}^{c}K_{HA}$ for a given class of functional group is remarkably similar in value regardless of the source of fulvic acid and regardless of chemical parameters such as the concentration of fulvic acid or the ionic strength. No significant monotonic variation of log ${}^{c}K_{HA}$ with the degree of protonation α_p was observed for any set of titration data, either (so long as α_p was not in the "overlap ranges," $0 < \alpha_p < 0.1$ and $0.9 < \alpha_p < 1$, where more than one class of functional group was being protonated). Thus it may be concluded that log ${}^{c}K_{HA}$ has the values 3.9, 6.5, and 9.4, within the experimental errors listed in Table II.10, on the basis of 259, 281, and 282 determinations for the acid functional groups of classes II, III, and IV, respectively. The first and last of these overall mean values turn out to compare well with the protonation constants determined by Gamble (1972) in an ionic medium of 0.1 mol/kg KCl for fulvic acid extracted from naturally occurring soil organic matter. However, Gamble's more acidic class of functional group exhibited a smaller value of log ${}^{c}K_{HA}$ (near 3) than did the class II groups, on the average, and showed a strong dependence on α_p. The very weakly acidic class of functional group he investigated, on the other hand, had a value of log ${}^{c}K_{HA}$ equal to 9.2 and showed no dependence on α_p, in agreement with what was observed in the present study for the class IV functional group.

The numbers of titratable protons in each class of acidic functional group are listed in columns 6, 9, and 12 of Table 43; the total numbers of titratable protons for the three classes are listed in column 14 of Table 43. It may be seen that, at a fixed ionic strength, the number of titratable protons increases with a decrease in FA concentration in the cases of the class III and class IV functional groups. The class II

TABLE 43. CONDITIONAL-PROTONATION CONSTANTS AND ENDPOINT DATA OBTAINED FROM TITRATION CURVES AT 25°C FOR FULVIC ACIDS A AND B1.

Exp. no.	Fulvic acid	Fu_T	I*	log K_{II} †	n_H^{II}	%	log K_{III} †	n_H^{III}	%	log K_{IV} †	n_H^{IV}	%	n_H ‡
		g/liter			meq/g			meq/g			meq/g		meq/g
1	A	1.0	0.2	3.96 ±0.37 (21)	0.413	36.6	6.22 ±0.11 (9)	0.357	31.6	9.41 ±0.24 (18)	0.359	31.8	1.129
2	A	1.0	0.2	3.90 ±0.18 (7)	0.372	33.1	6.35 ±0.14 (15)	0.388	34.5	9.358±0.031 (11)	0.364	32.4	1.124
3	A	0.5	0.2	3.95 ±0.17 (15)	0.422	24.8	6.393±0.096 (13)	0.712	41.9	9.39 ±0.26 (11)	0.567	33.3	1.701
4	A	0.5	0.2	3.814±0.080 (16)	0.487	30.3	6.396±0.052 (14)	0.579	36.1	9.406±0.074 (13)	0.540	33.6	1.606
5	A	0.5	0.1	3.887±0.077 (22)	0.620	33.3	6.65 ±0.26 (27)	0.720	38.7	9.44 ±0.11 (26)	0.521	28.0	1.861
6	A	0.5	0.1	3.805±0.047 (27)	0.633	35.4	6.589±0.099 (12)	0.620	34.7	9.29 ±0.10 (15)	0.536	30.0	1.789
7	A	0.25	0.1	3.68 ±0.13 (21)	0.537	18.7	6.67 ±0.26 (25)	1.419	49.4	9.390±0.078 (24)	0.916	31.9	2.872
8	A	0.25	0.1	3.748±0.078 (14)	0.476	20.4	6.48 ±0.25 (20)	0.960	41.1	9.383±0.095 (19)	0.902	38.6	2.338
9	B1	1.0	0.1	4.059±0.027 (18)	0.614	31.3	6.549±0.25 (19)	0.797	40.6	9.295±0.070 (20)	0.552	28.1	1.963
10	B1	1.0	0.1	4.014±0.053 (27)	0.601	31.4	6.577±0.071 (20)	0.774	40.4	9.338±0.079 (19)	0.539	28.2	1.914
11	B1	0.5	0.1	4.129±0.051 (19)	0.485	22.8	6.556±0.049 (27)	0.928	43.6	9.484±0.044 (14)	0.715	33.6	2.128
12	B1	0.5	0.1	4.021±0.050 (21)	0.569	28.8	6.615±0.053 (29)	0.902	45.7	9.307±0.089 (25)	0.502	25.4	1.973
13	B1	0.5	0.1	3.779±0.066 (15)	0.659	15.1	6.586±0.067 (23)	2.069	47.4	9.614±0.054 (39)	1.64	37.5	4.368
14	B1	0.5	0.1	3.625±0.16 (16)	0.600	15.6	6.364±0.061 (28)	1.83	47.5	9.558±0.061 (28)	1.42	36.9	3.853

* Ionic strength

† Uncertainties reported are standard deviations for the number of calculations of K_{HA} shown in parentheses.

‡ The sum of columns 6, 9, and 12.

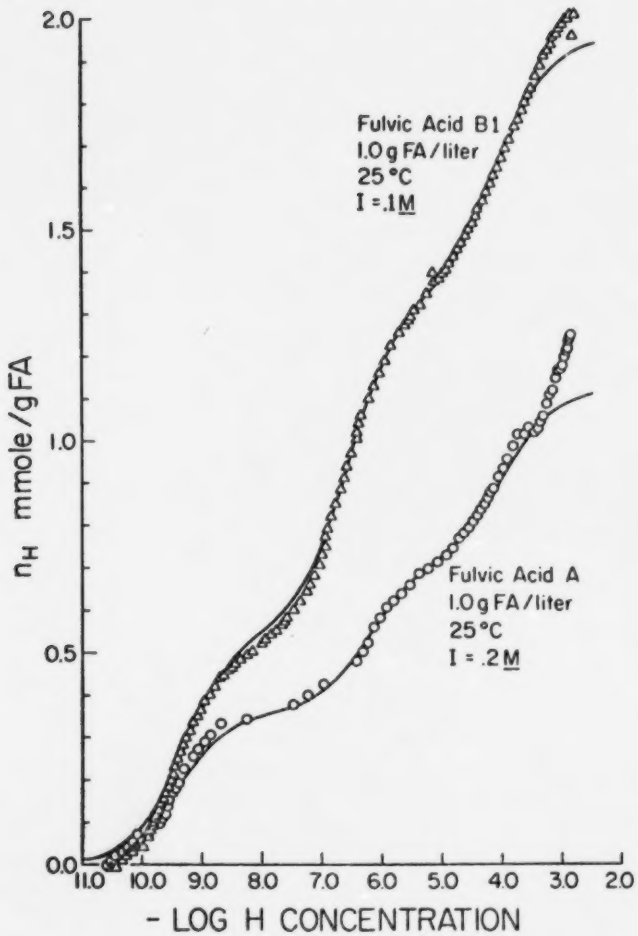

Fig. 14. Potentiometric titration curves for fulvic acids A and B1 at 25° C. The lines through the data points were computed using Eq. 2.1 and the data in rows 1 through 9 in Table 43.

functional groups sometimes appear to show the reverse trend, evidently as a result of counter-ion condensation (Sposito and Holtzclaw, 1977), although the total number of titratable protons still increases with decreasing FA concentration. For a fixed concentration of FA, the numbers of titratable protons show a slight increase overall with a decrease in ionic strength, due primarily to the effect of ionic strength on the class II functional groups. These two general trends are consistent with the idea (Sposito et al., 1977) that association of mean fulvic acid units through hydrogen bonding decreases the number of titratable protons, since both an increase in FA concentration and in ionic strength would tend to promote molecular association and coagulation.

There also is a time-dependent aspect of the association among mean fulvic acid units through hydrogen bonding, as may be seen through an examination of the last four rows of data in Table 43. Experiments 11 and 12 differed from 13 and 14 only in the amount of time that elapsed between the preparation of the fulvic solution from lyophilized material and the measurement of the titration curve. In the cases of Exp. 13 and 14, this time was about 20 hours, whereas in the cases of Exp. 11 and 12 it was about 10 days. The dramatic decrease observed in the numbers of titratable protons for all three classes of functional group as the "standing time" increased suggests strongly that molecular association among the FA units has an important kinetic feature, at least at the pH values of the K/H-fulvate solutions. This trend is illustrated in detail in Fig. II.14, which is a plot of the titration data for Exp. 12 and 13.

The percentages of titratable protons in each class of weakly acidic functional group are listed in columns 7, 10, and 13 of Table 43. An examination of these data shows that quite generally the changes in chemical factors that promote molecular association also promote significant decreases in the percentages of titratable protons in the class III functional groups. The effects are present, but less pronounced for the class IV functional groups as well. This observation indicates that molecular association among the mean FA units principally involves the class III functional groups in hydrogen bonds.

Calcium complexation

The complexation reactions of bivalent metal cations with the organic acids that are expected to be found in soil solutions have become a subject of considerable interest in recent years (Gamble and Schnitzer, 1973; Stevenson, 1976; Gamble, 1977). A variety of experimental methods exists for the investigation of these reactions (see, e.g., Rossotti and Rossotti, 1961). But the applications of some of the available methods that have appeared in the literature of soil chemistry all too often have been questionable because of a failure to demonstrate that the assumptions which underlie the chosen experimental approach are in fact satisfied (see, e.g., MacCarthy and Mark, 1976; Crosser and Allen, 1977; MacCarthy, 1977). The root of the difficulty in these cases has been the need to distinguish

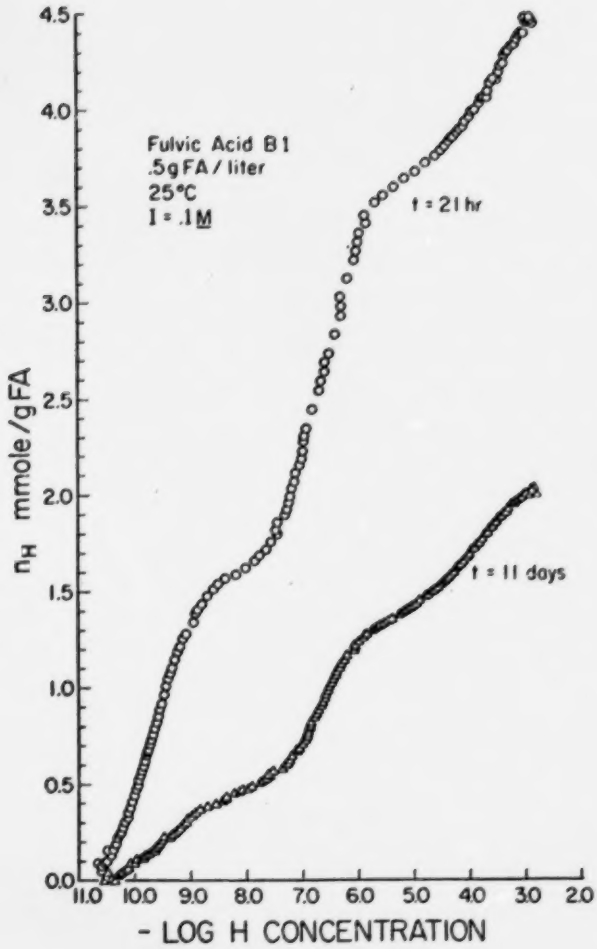

Fig. 15. The effect of standing time in solutions (t) on the titration curve for fulvic acid B1.

clearly between those methods for studying metal complexation reactions that require a prior knowledge of the nature of the metal-organic complex formed and those methods that do not.

Logically, the nature of metal-organic complexes should be determined, at least to the extent of establishing what number of complexes form and what are their stoichiometric coefficients, before attempting to determine complex stability constants. Basic information about complexes can be obtained from measurements of the appropriate formation function, which is the average number of moles of ligand bound per mole of central group or nucleus (Rossotti and Rossotti, 1961; Sillen, 1972). The formation function, in general, will depend on temperature, ionic strength, pH, the concentration of ligand, and the concentration of the central group. The experimentally-observed variation of the formation function with the last two properties listed may be used to obtain information about the number of complexes formed and their stoichimetric coefficients, e.g., whether they are polynuclear or mononuclear with respect to the central group (Sillen, 1972). Such information must be available before any method for determining stability constants can be utilized.

The complexes formed between Ca^{2+} and fulvic acid extracted from sewage sludge were investigated by potentiometric titration of K/H-fulvate with $Ca(NO_3)_2$ at pH 7 and 25°C, in an ionic medium of 0.1N KNO_3. Formation functions, giving the number of moles of Ca bound per mole of K/H-fulvate, were calculated from the titration data and plotted against the concentration of Ca^{2+}, with the concentration of K/H-fulvate being a fixed parameter for each plot. The molarity of K/H-fulvate, which was held rigorously constant during each titration, was determined with the help of separate experiments in which the number-average molecular weight of the K/H-fulvate sample employed was measured by vapor pressure osmometry. The formation functions were interpreted as evidence of: (i) a relatively strong ion pair that is formed between Ca^{2+} and the most acidic functional groups in fulvic acid, and (ii) a weaker ion pair that is formed between Ca^{2+} and the more weakly acidic functional groups. The properties of the latter complex depend both on pH and on the concentration of fulvic acid, since these variables in part determine the number of ionized, weakly acidic functional groups that can react with Ca^{2+}. The Ca^{2+} ion was shown to have a modest ability to displace protons from undissociated acidic functional groups in sludge-derived fulvic acid.

Formation functions, describing the complexation of Ca by fulvic acid at 25°C and pH 7 in an ionic medium of 0.1 N KNO_3, are plotted in Fig. 16. For each curve shown, the molar concentration of Ca^{2+} is the independent variable while the concentration of K/H-fulvate is a parameter fixed at 0.25, 0.50, or 1.00 g/liter. The formation functions display three principal features which may be interpreted to give information about Ca-fulvic acid complexes under the conditions of the experiments.

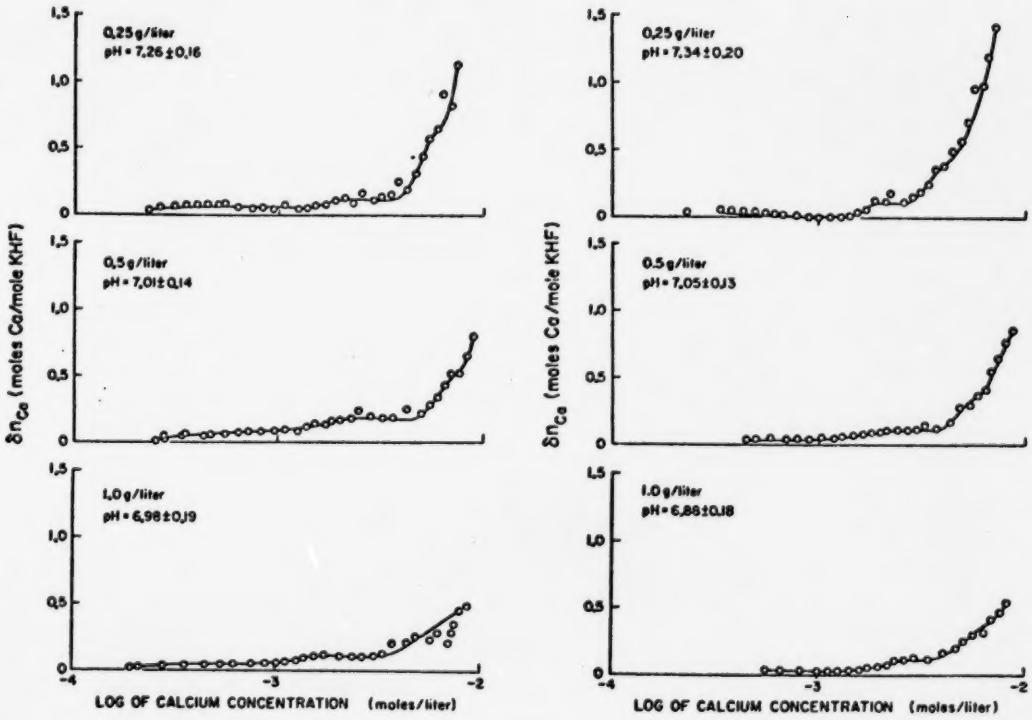

Fig. 16. Graphs of the formation function δn_{Ca} for the complexation of Ca^{2+} by fulvic acid at 25°C and pH 7 in an ionic medium of 0.1N KNO_3. The concentration of K/H-fulvate is a parameter for each curve shown.

The first important property of the formation functions is that they exhibit a low plateau at about 0.1 mole Ca/mole K/H-fulvate (see Table 44) that extends over the range of Ca^{2+} concentration between $10^{-2.7}$ M and $10^{-2.4}$ M, but is independent of the K/H-fulvate concentration. The value of the formation function, δn_{Ca}, at the plateau is about the same as the content of K in the K/H-fulvate (= 0.41 mmole K/g x 0.243 g/mmole fulvate). The funcational groups neutralized by K^+ in the K/H-fulvate are the ones that exchange H^+ readily for K^+ during the K-resin treatment of FA and, therefore, are expected to be strongly acidic. All of these considerations suggest that the plateau in n_{Ca} represents a Ca-fulvic acid complex in which one Ca^{2+} ion and one mean fulvate anion (in the sense of Sposito et al., 1977) participate. Indeed, if more than one fulvate anion were involved, the plateau feature would not have been independent of the K/H-fulvate concentration

TABLE 44. MEAN VALUES OF δN_{Ca} IN THE PLATEAU REGIONS SHOWN IN FIG. 16.

Fu_T (g/liter)	pH	δn_{Ca} at the plateau
0.25	7.34 ± 0.20	0.120 ± 0.006
0.25	7.26 ± 0.16	0.120 ± 0.027
0.50	7.05 ± 0.13	0.109 ± 0.004
0.50	7.01 ± 0.14	0.183 ± 0.007
1.0	6.98 ± 0.19	0.114 ± 0.006
1.0	6.88 ± 0.18	0.121 ± 0.008

(Cf. Sposito et al, 1977). A mean fulvate anion in fulvic acid B1 bears about 0.1 electronic charges that are associated with strongly acidic functional groups. Evidently these groups can complex relatively strongly with Ca^{2+} to form ion pairs. Since the concentrations of the inorganic species $CaOH^+$ and $CaNO_3^+$ in the titrated solutions always amounted to <7% of the total Ca concentration (according to a calculation made by GEOCHEM), one may conclude that the Ca-fulvic acid complex under consideration involves primarily Ca^{2+} and, therefore, would have a charge equal to about 0.1 protonic charges if the other acidic functional groups on the mean fulvic acid molecule were to remain undissociated.

A second characteristic feature of δn_{Ca} is the inflection point that occurs in the range 0.3 to 0.7 mole Ca/mole K/H-fulvate as the concentration of K/H-fulvate decreases from 1.0 to 0.25 g/liter. At a concentration of 0.5 g/liter and at pH 7, fulvic acid B1 should have dissociated about 0.7 moles H^+ per mole from its Class I, II, and III functional groups (Cf. Sposito et al., 1977, Fig. 2). This value compares with the average value of δn_{Ca} (0.5 mole Ca/mole fulvate) at the inflection point for a K/H-fulvate concentration of 0.5 g/liter, indicated in Fig. 16. It appears, then, that the inflection point corresponds to a 1:1 complex between Ca^{2+} and some of the dissociated acidic functional groups in fulvic acid B1. This complex is weaker than that formed between Ca^{2+} and the strongly acidic functional groups and is expected to depend on pH, since the number of dissociated functional groups depends on pH. The dependence of δn_{Ca} at the inflection point on the K/H-fulvate concentration (Fig. 16) is a reflection of the same concentration dependence shown by the numbers of dissociable protons in fulvic acid B1 (Sposito et al., 1977). As the K/H-fulvate concentration increases, the protonated functional groups on different molecules associate more through hydrogen bonding and the number of titratable protons decreases.

The third significant characteristic of δn_{Ca} is its relatively sharp rise, after the inflection point, as the concentration of Ca^{2+} increases. This rise may be attributed to two causes: the complexation of Ca by ionized functional groups that did not react when $[Ca^{2+}]$ was smaller, and the exchange of Ca^{2+} for H^+ on functional groups that are not normally ionized at pH 7. That Ca^{2+} replaces H^+ appreciably when $[Ca^{2+}]$ approaches 10^{-2}M may be inferred from Fig. 17, which shows representative plots of the volume of KOH/KNO_3 solution added during titration, in order to maintain constant pH, vs. δn_{Ca}. The particularly steep rise in δn_{Ca} shown in Fig. 16, when the K/H-fulvate concentration was fixed at 0.25 g/liter and $[Ca^{2+}] = 10^{-2.2}$M, evidently is associated with a similarly strong increase in the amount of base added to neutralize some of the exchanged protons that come into solution. It may be noted also that protons are exchanged even during the ascent of δn_{Ca} to the inflection point; this fact helps to explain why the inflection point is not more pronounced. At a concentration of 0.5 g/liter, K/H-fulvate B1 can dissociate about 1.1 mole H^+ per mole (= 243 g/mole ÷ 221 g/equiv) according to Table 2 in Sposito et al. (1977). The maximum value of δn_{Ca} accordingly would be about 1.1 mole Ca per mole K/H-fulvate if 1:1 complexes formed. This value is consistent with the data for 0.5 g/liter K/H-fulvate that are plotted in Fig. 17. The left-hand set of graphs, in particular, suggests that a plateau in δn_{Ca} is forming at about 1 mole Ca per mole K/H-fulvate when $[Ca^{2+}]$ is equal to $10^{-2.13}$M, the largest Ca^{2+} concentration achieved during the titration experiment.

Copper Complexation

The study of the complexes formed between Cu^{2+} and fulvic acid

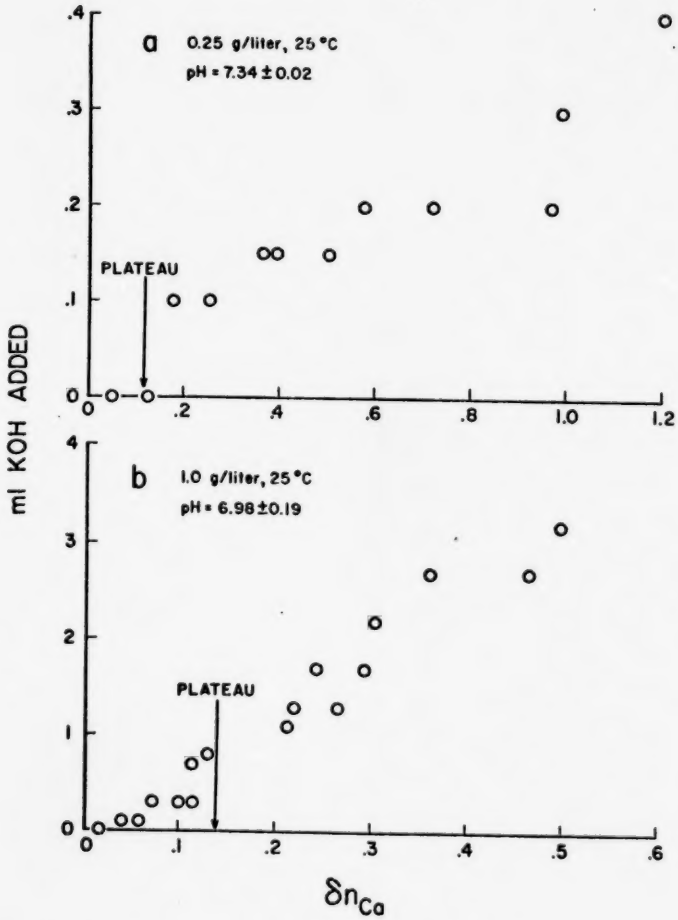

Fig. 17. The volume of KOH added to maintain constant pH during the titration of K/H-fulvate with $Ca(NO_3)_2$, plotted as a function of δn_{Ca}; (a) Fu_T = 0.25 g/liter, and (b) Fu_T = 1.0 g/liter.

continues to be a subject of considerable interest in the trace metal chemistry of soil solutions and other natural waters. With respect to equilibrium phenomena, a principal means of characterizing Cu^{2+} - fulvic acid complexes is through the determination of the conditional complex stability constant (see, e.g., Buffle et al., 1977). This parameter gives an average measure of the complexation reactions in fulvic acid solutions and is a function of temperature, pressure, and the solution composition. It can be calculated from data representing the equilibrium state of an aqueous solution of Cu and fulvic acid, provided that three criteria are met: (i) the average stoichiometry of the complexes formed is known, (ii) the activities or concentrations of Cu^{2+} and the mean fulvate anion have been determined, and (iii) the activity or concentration of the average Cu-fulvic acid complex is available. The criterion (iii) can be satisfied in several ways, but in any of them the proper choice of a background ionic medium in which to follow the reaction between Cu^{2+} and fulvic acid is greatly important. Studies of Cu^{2+} complexation by fulvic acid have been carried out in Cl systems (Gamble et al., 1970; Schnitzer and Hansen, 1970; Gamble and Schnitzer, 1973; Stevenson et al., 1973), in NO_3 systems (Cheam, 1973; Cheam and Gamble, 1974; Buffle et al., 1977; Shuman and Woodward, 1977), and in ClO_4 systems (Manning and Ramamoorthy, 1973).

Of these three background ionic media, the Cl systems perhaps should be avoided in general because they offer the problem of (i) the possibility of K^+ complexation by the fulvate anions (Gamble, 1973), (ii) a significant presence of Cl complexes with Cu^{2+} at the typical ionic strength of 0.1M (see, e.g., Mattigod and Sposito, 1977) and (iii) Cu^{2+} reduction to Cu^+ at the Cu electrode surface if that ion-selective electrode is employed to determine the Cu^{2+} activity (Westall et al., 1977; Hibbert et al., 1978). Potassium ions have been shown to form complexes with soil-derived fulvic acid in aqueous solutions with K^+ concentrations > 0.004M and pH > 7 (Gamble, 1973). There is some evidence, on the other hand, that K^+ does not form complexes with sewage sludge-derived fulvic acid in solutions at pH 4.5 even when the concentration of K^+ is 0.2M (Sposito et al., 1977). If K^+ is able, under certain conditions, to compete effectively with Cu^{2+} for metal-complexing functional groups in fulvic acid, then the interpretation of formation functions and conditional stability constants for Cu^{2+} complexation would become ambiguous. The presence of $CuCl^+$ ion pairs in addition to Cu^{2+}-fulvic acid complexes would also complicate matters greatly, since the usual measurement of the concentration of complexed Cu as the difference between the total concentration of Cu and that of Cu^{2+} in solution would then give the sum of the concentrations of Cu^{2+}-fulvate, $CuCl^+$, and mixed $CuCl^+$-fulvate complexes.

An appreciation of these difficulties has prompted the recent use of NO_3 ionic media instead of Cl ionic media. However, the results obtained by Hester and Plane (1964) in their study of the Raman spectra of aqueous solutions of metal nitrates puts even this choice of ionic medium in some doubt. Hester and Plane (1964) investigated the shift in NO_3^- vibrational frequencies brought on by the distortion of the symmetry of the anion that accompanies metal complex formation

through its oxygen atoms. They found that the deformation of NO_3^- in the presence of Cu^{2+} was significantly greater than that in the presence of Ca^{2+}. Since Ca^{2+} is known to form a weak ion pair with NO_3^- that has a thermodynamic stability constant (at 25°C) equal to about $10^{0.3}$ (see, e.g., Sposito et al., 1978), the results of Hester and Plane (1964) suggest that the ion pair $CuNO_3^+$ may be present in NO_3 ionic media with even a greater stability. If $CuNO_3^+$ were relatively abundant at ionic strengths near 0.1M in NO_3 ionic media, then clearly the results of studies on Cu^{2+}-fulvic acid complexes carried out in such media would be suspect.

The possible adverse effect of $CuNO_3^+$ ion pairs on studies of the complexes formed between Cu(II) and fulvic acid extracted from sewage sludge was investigated by potentiometric titration of 2×10^{-3}M K/H fulvate with $Cu(NO_3)_2$ and $Cu(ClO_4)_2$, at pH 5 and 25°C, in ionic media of 0.1M KNO_3 or $KClO_4$, respectively. It was shown that the degree of complexation of Cu^{2+} in the NO_3 medium was always significantly greater than that in the ClO_4 medium for total Cu concentrations in the range 10^{-4}M to 10^{-2}M. This result was interpreted as evidence for significant concentrations of $CuNO_3^+$ ion pairs and mixed $CuNO_3$-fulvate complexes in the NO_3 medium. Further support for the existence of $CuNO_3^+$ in the NO_3 medium was obtained through a successful calculation of the thermodynamic stability constant for this ion pair that employed data from blank titrations with $Cu(NO_3)_2$ and $Cu(ClO_4)_2$. It was concluded that ClO_4 ionic media should be used instead of NO_3 ionic media in studies of Cu(ii) complexation with the functional groups of fulvic acid.

A comparison of the fulvate titrations carried out in ClO_4 and NO_3 ionic media may be made conveniently through a log-log plot of the degree of complexation parameter, β, versus the total concentration of Cu added to the fulvate solution. The parameter is defined by the expression (Buffle et al., 1977):

$$\beta \equiv Cu_T 10^{(E_o-E)/B} \qquad (25)$$

where Cu_T is the total concentration of Cu added, E is the corresponding EMF measured by the Cu electrode, and E_o and B are the Nernst equation parameters for the electrode. The quantity β gives a numerical measure of the extent of Cu complexation, in that, if E_o and B are determined for blank titration solutions containing only the Cu^{2+} form of Cu, β is equal to the ratio $Cu_T/[Cu^{2+}]$ and will be larger the more Cu is in complexed form. As Cu_T increases, for a fixed concentration of complexing ligand, it is expected that β will approach the value 1.0.

The values of β for a set of four titration experiments performed at 25°C in a 0.1M NO_3 or ClO_4 ionic medium containing K/H fulvate maintained at the constant concentration of 0.5 g/liter (2×10^{-3}M, Sposito et al., 1978a) are graphed in Fig. 18. It may be seen that β does indeed decrease toward the value 1.0 as Cu_T increases in all the titration experiments. However, the curves for the titrations carried out in a NO_3 medium lie significantly above those for the titrations

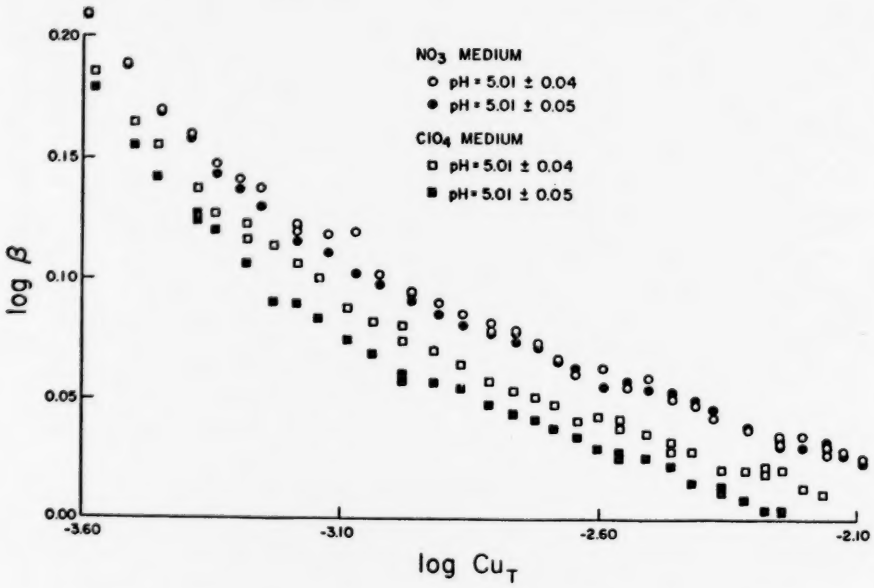

Fig. 18. A log-log plot of the complexation parameter β against the total Cu concentraiton, as determined by the potentiometric titration of 2 X 10^{-3}M K/H fulvate at 25° C in either NO_3 or ClO_4 ionic media. Open and filled symbols having the same shape refer to replication of the same titration experiment.

carried out in a ClO_4 medium. Since there is no evidence for ClO_4 complexes with Cu at the pH value and ionic strength of the titration experiments (Cf. Smith and Martell, 1976) and given that no significant difference in liquid junction potentials exists, it may be inferred that the difference between the two sets of curves in Fig. 18 is caused by complexes between Cu^{2+} and NO_3^-, including mixed $CuNO_3^+$-fulvate complexes, in the NO_3 ionic medium.

If $CuNO_3^+$ ion pairs are present in the NO_3 ionic medium, it should be possible to calculate a value of the thermodynamic stability constant, K, for these ion pairs using the data from the blank $Cu(NO_3)_2$ and $Cu(ClO_4)_2$ titrations, again assuming that liquid junction potentials are the same in both experiments. The procedure for making this calculation is straightforward. The value found using this procedure was log K = 0.44 ± 0.13 at 25°C. This result compares well with log K = 0.54 calculated by Federov et al. (1973), who determined conditional stability constants, ${}^cK$, for $CuNO_3^+$ at I = 0.5M, 1.0M, and other ionic strengths up to 4.0M, then fit their data to the empirical relation.

$$\log {}^cK = \log K - \frac{4AI^{\frac{1}{2}}}{1 + BaI^{\frac{1}{2}}} + bI \qquad (26)$$

where A and B are the Debye-Huckel parameters, a = 4.9A, and b = 0.13 liter/mole. The use of this equation might be questioned on fundamental grounds because the distance parameter a should be 6A for Cu^{2+} (see, e.g., James, 1976, p. 256) and because ionic strengths up to 4.0 M were employed to determine b. If the Davies equation is used instead to convert the values of ${}^cK$ reported by Fedorov et al. (1973) for I = 0.5M and 1.0M directly to values of K, the result is log K = 0.40 + 0.01. This value is in excellent agreement with log K determined in the present investigation. No other published data on K for $CuNO_3^+$ than those of Fedorov et al. (1973) seem to be available (Smith and Martell, 1976).

The graph of log β vs. log Cu_T for the NO_3 medium should now be corrected for the fact that the calibration of the Cu electrode in KNO_3 actually refers to a linear correlation between EMF and log[$Cu(NO_3)_2$] instead of between EMF and log[Cu^{2+}]. This correction may be initiated by computing α_{Cu} for each point of the $Cu(NO_3)_2$ blank titration, multiplying it by the corresponding [$Cu(NO_3)_2$], then redoing the linear correlation of EMF with log[Cu^{2+}] to get the correct values of E_o and B. Equivalently, β may be recomputed for the fulvate titrations in the NO_3 ionic medium simply by using data from the calibration of the electrode in $KClO_4$. The results of the corrected calculation of β are shown in Fig. 19. It is seen that the true curve for log β describing the fulvate titration in the NO_3 ionic medium lies considerably above those for the titrations in the ClO_4 ionic medium. For example, at $Cu_T = 10^{-3}$ M, the value of β deduced from the graph is about 1.38 in the NO_3 medium and 1.19 in the ClO_4 medium, indicating that about 28% of the Cu is in complexed form in the NO_3 medium whereas only about 13% of the Cu is in complexed form in the ClO_4 medium. The difference evidently represents the presence of $CuNO_3^+$ ion pairs and $CuNO_3^+$-fulvate complexes in the NO_3 ionic medium.

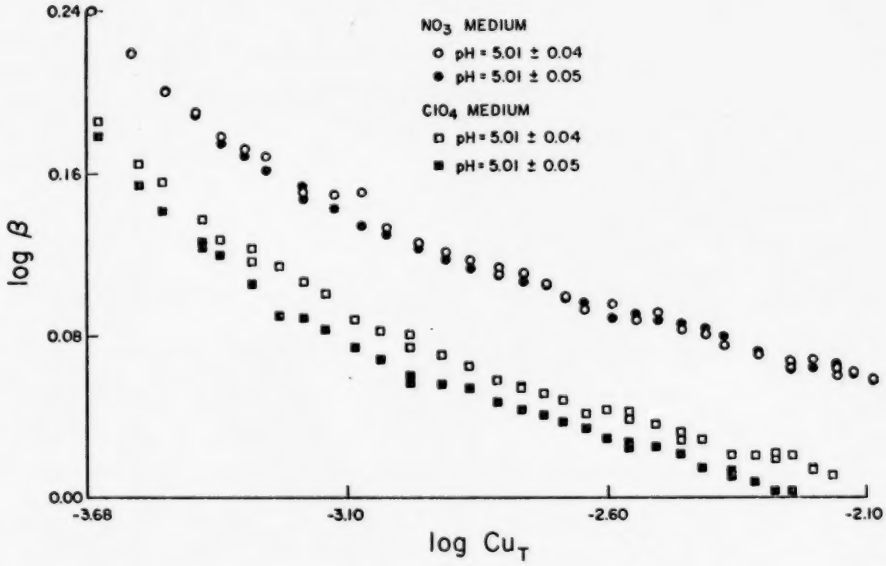

Fig. 19. Corrected log-log plot of β against Cu_T as determined by the titration of K/H fulvate in a NO_3 ionic medium. The curves for the ClO_4 ionic medium are identical with those shown in Fig. 18.

Copper(II) complexes with fulvic acid extracted from soil have been studied a great deal in the past few years and a variety of methods has been applied to measure their stability constants. A representative summary of the recent work in this area is presented in Table 45.

Two important general aspects of the previous investigations of Cu(II)-fulvic acid complexes are brought to mind through an examination of Table 45. First, most of the studies have been carried out in Cl or NO_3 background media and some have been done at pH values above 5. This means that the complexes formed most probably included mixed Cu(II)-inorganic ligand-organic ligand complexes instead of only Cu^{2+}-fulvic acid complexes, where the inorganic ligand could be Cl^-, NO_3^-. and/or OH^-. Since Cu^{2+} forms ion pairs significantly with Cl^- and NO_3^- and begins to hydrolyze extensively at pH values near 6, the formation of mixed complexes in 0.1 M background media or at pH values much above 5 is almost a certainty (Sposito and Holtzclaw, 1979). With the exception of the work of Manning and Ramamoorthy (1973), which was carried out in an acidic ClO_4 medium, it appears that Cu^{2+}-fulvic acid complexes *per se* actually have not yet been investigated.

The second general aspect of the work summarized in Table 45 is the tendency to treat fulvic acid as a monofunctional ligand in its complexation reaction with Cu^{2+}. Although this approach is not invalid, it produces a conditional stability constant that exhibits the undesirable property of varying strongly with the extent of Cu complexation per mole of fulvic acid (Cheam, 1973; Bresnahan et al., 1978). This strong variation is a reflection of the fact that fulvic acid is better represented as a polyfunctional ligand in the same sense as a protein (see, e.g., Tanford, 1961, Chap. 8). In the case of fulvic acid extracted from sewage sludge, polyfunctionality is exhibited with respect to proton complexation (Sposito et al., 1977) and calcium complexation (Sposito et al., 1978). Therefore, it would seem that a method capable of identifying different classes of metal complexing groups and determining their particular stability constants is to be preferred over one that lumps all the groups together into a single, variable stability parameter. Manning and Ramamoorthy (1975) and Bresnahan et al. (1978) have employed the conventional Scatchard plot method (Scatchard et al., 1957) to analyze Cu(II)-fulvic acid complexes according to classes and to calculate their stabilities. This method was developed especially for polyfunctional macromolecules and, therefore, would appear to be pertinent to the study of Cu^{2+} complexation by fulvic acid extracted from sewage sludge.

The complexes formed between Cu^{2+} and fulvic acid extracted from sewage sludge were investigated by potentiometric titration of K/H fulvate with $Cu(ClO_4)_2$ at pH 5 and 25°C, in an ionic medium of 0.1 M $KClO_4$. Formation functions, giving the number of moles of Cu^{2+} bound per mole of K/H fulvate, were calculated from the titration data and plotted against the molar concentration of Cu^{2+}, with the concentration of K/H fulvate being a fixed parameter for each plot. These functions were analyzed by the Scatchard plot method and were interpreted as evidence of: (i) a relatively strong 1:1 complex (log ^cK =

TABLE 45. RESUME OF SOME RECENT MEASUREMENTS OF CONDITIONAL STABILITY CONSTANTS FOR Cu(II) COMPLEXATION BY SOIL-DERIVED FULVIC ACID AT 25°C.

Investigator	Method	Ionic background	pH	Assumed complexation reaction
Gamble, Schnitzer, and Hoffman (1970)	Ion exchange	0.1 m KCl	3	$HFu^- + Cu^{2+} = CuFu + H^+$
Stevenson, Krastznov, and Ardakani (1973)	Potentiometric titration	0.1 M KCl	4-5	$2\ HFu + Cu^{2+} = CuFu_2 + 2H^+$
Cheam (1973)	Potentiometric titration	0.1 M $NaNO_3$	3-5	$HFu^- + Cu^{2+} = CuFu + H^+$
Manning and Ramamoorthy (1973)	Potentiometric titration	0.1 M $NaClO_4$	2-5	$Fu^{2-} + Cu^{2+} = CuFu$
Cheam and Gamble (1974)	Potentiometric titration	0.1 M $NaNO_3$	3-5	$Fu^{2-} + Cu^{2+} = CuFu$
Mantoura and Riley (1975)	Gel chromatography	0.01 M NaCl/TRIS	8	$A_i + Cu^{2+} = CuA_i$ (i=1,2)
Buffle, Greter, and Haerdi (1977)	Potentiometric titration	0.1 M NaNO	3-7	$aH_xFu + Cu^{2+} = CuFu_a + axH^+$ (a=1,2)
Bresnahan, Grant, and Weber (1978)	Potentiometric titration	0.1 M KNO_3	4-6	$A_i + Cu^{2+} = CuA_i$ (i=1,2)

3.9) that is formed between Cu^{2+} and the most acidic functional groups in fulvic acid and (ii) a weaker set of complexes (log ^{c}K = 2) that is formed between Cu^{2+} and the more weakly acidic functional groups acting as both unidentate and bidentate ligands.

Formation functions, depicting the number of moles of Cu^{2+} complexed per mole of K/H fulvate at 25°C and pH 5 in an ionic medium of 0.1 M $KClO_4$, are plotted in Fig. 20 and 21. For each set of data shown, the molar concentration of Cu^{2+} is the independent variable, with the concentration of K/H fulvate fixed at 0.5 g/liter (2.06×10^{-3} M) or 0.25 g/liter (1.03×10^{-3} M). It is evident in Fig. 20 and 21 that good reproducibility was obtained in duplicate titration experiments and that the extent of complexation of Cu^{2+} by K/H fulvate at a given concentration of Cu^{2+} increases as the fulvate concentration decreases. This type of dependence of the formation function on the fulvate concentration also was noted in the cases of H^{+} and Ca^{2+} complexation by K/H fulvate (Sposito et al., 1977, 1978a). As was true for protons and Ca^{2+}, the complexation of Cu^{2+} by K/H fulvate appears to depend on the extent to which protonated functional groups are not associated through hydrogen bonding which is enhanced as the fulvate concentration increases (Sposito et al., 1977).

In the case of Ca^{2+} complexation by K/H fulvate (Sposito et al., 1978a), it was found that two general classes of complexing functional group could be identified by simple inspection of the formation function. One of these classes formed a relatively strong, 1:1 complex with up to 0.1 mole Ca^{2+} per mole K/H fulvate regardless of the fulvate concentration. This class could be associated with the most strongly acidic functional groups in K/H fulvate. The other class was associated with the more weakly acidic functional groups. It did not exhibit a pronounced inflection point or plateau in the formation function. The extent of Ca^{2+} complexation (also 1:1) by this class of sites depended on the fulvate concentration and on the ability of Ca^{2+} to displace protons.

In the case of Cu^{2+} complexation by K/H fulvate, Fig. 20 and 21, no pronounced inflection points exist in the formation function, although a hint of an inflection point does appear when $n_{Cu} \simeq$ 0.2 mol Cu^{2+}/mol K/H fulvate. When the classes of complexing functional groups cannot be distinguished by strong inflection points, it is still possible to deduce their properties through a Scatchard plot analysis (Scatchard et al., 1957). A conventional Scatchard plot of the data from Expt. 1 in Fig. 20 is shown in Fig. 22 (upper curve). The plot is asymptotically a straight line both as $n_{Cu} \rightarrow 0$ and as $n_{Cu}/[Cu^{2+}] \rightarrow 0$. If there are only two classes of complexing groups, a Scatchard plot of n^{1}_{Cu}, the formation function for the second class of groups, also must be a straight line. This behavior is substantiated in the lower curve of Fig. 22.

The numerical values of the parameters n_1, $^{c}K_1$, n_2, and $^{c}K_2$ as derived from Scatchard plots of the data in Fig. 20 and 21, are listed in Table 46. The parameter n_1, the number of moles of complex-

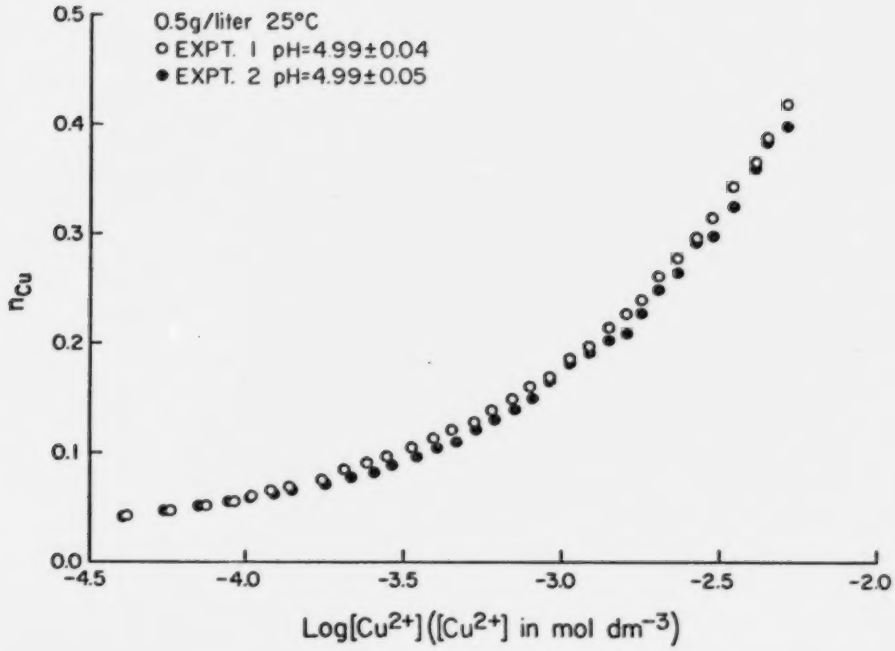

Fig. 20. Formation function for Cu^{2+} complexation by 0.5 g/liter K/H fulvate at pH 5.0 in 0.1 M $KClO_4$.

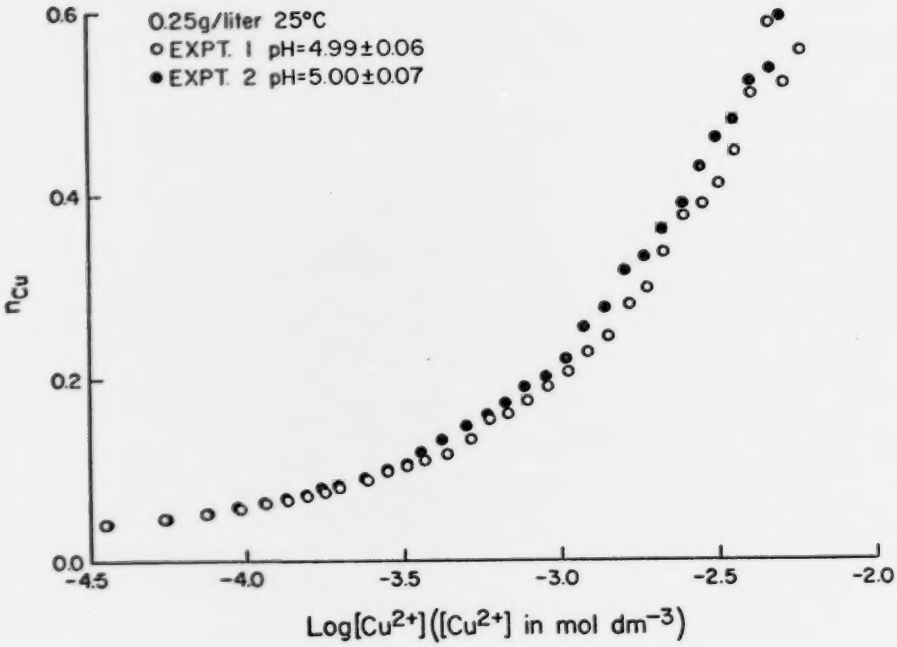

Fig. 21. Formation function for Cu^{2+} complexation by 0.25 g/liter K/H fulvate at pH 5.0 in 0.1 M $KClO_4$.

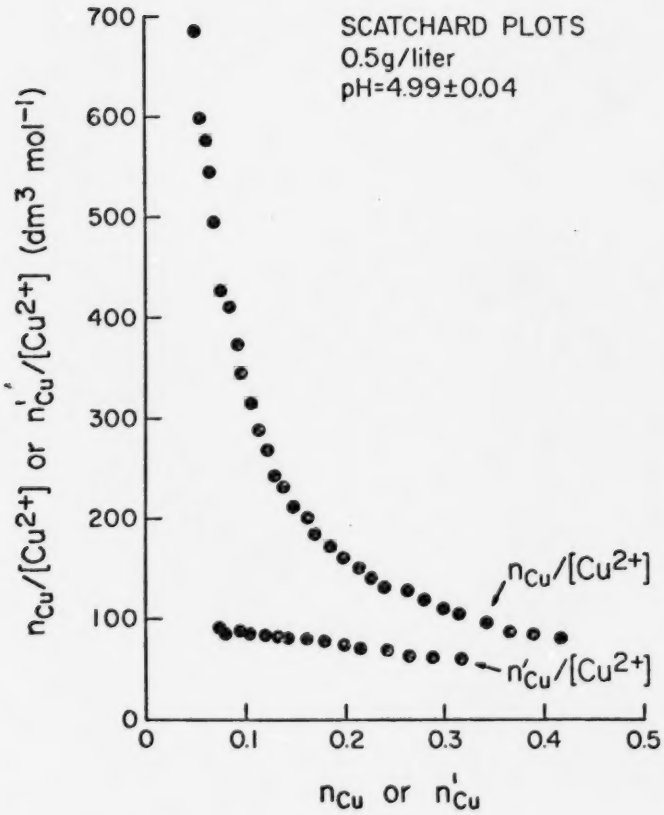

Fig. 22. Scatchard plots of the data from Exp. 1 in Fig. 20 (upper curve) and of calculated n'_{Cu}.

TABLE 46. COMPOSITE CONDITIONAL STABILITY CONSTANTS AND NUMBERS OF COMPLEXATION SITES FOR Cu^{2+} BINDING BY FULVIC ACID AT 25°C AND pH 5.0 in 0.1 M $KClO_4$.

Fu_T	n_1	log $^cK_1$	n_2	log $^cK_2$
g/liter				
0.50	0.104	3.85	0.803	2.09
0.50	0.087	4.07	0.758	2.14
0.25	0.105	3.96	1.33	1.96
0.25	0.110	3.79	1.13	2.14

ing groups per mole of K/H fulvate which form the stronger complexes with Cu^{2+}, is equal to 0.1 regardles of the fulvate concentration. This value is precisely the same as the number of moles of strongly acidic functional groups per mole of K/H fulvate and is the same as the maximum number of moles of Ca^{2+} complexed by the more reactive groups in one mole of K/H fulvate (Sposito et al., 1978a). Moreover, there is no significant difference among the values of log $^cK_1$ in Table 46. At the higher fulvate concentration, log $^c\bar{K}_1 = 3.97 \pm 0.11$, and at the lower concentration, log $^c\bar{K}_1 = 3.88 \pm 0.08$. (The overbar refers to an arithmetic average.)

The parameter n_2, on the other hand, does depend on the fulvate concentration. At the higher concentration, $\bar{n}_2 = 0.78 \pm 0.2$, whereas at the lower concentration, $\bar{n}_2 = 1.2 \pm 0.1$. The number of moles of ionized, weakly acidic functional groups in K/H fulvate at pH 5 and a fulvate concentration of 0.5 g/liter can be estimated with the help of the data in Table 43 (Expt. 13 and 14). This value is 0.156 ± 0.003, most of which is contributed by the Class II acidic functional groups. The parameter n_2 is much larger than this, which indicates that Cu^{2+} does not complex only with ionized functional groups. It is possible that the slight inflection at $n_{Cu} \simeq 0.2$ in Fig. 20 in fact reflects the contribution of the ionized, weakly acidic groups and that n_2 includes contributions from these groups as well as nonionized groups. The total number of moles of weakly acidic groups per mole of K/H fulvate at a fulvate concentration of 0.5 g/liter is 1.0 (Sposito et al., 1977). The parameter n_2 falls below this upper limit, either because not all of the non-ionized groups can complex Cu^{2+} effectively or because some of the Cu^{2+} complexes with pairs of functional groups. In the case

of Ca^{2+}, the upper limit of 1:1 complexation by the second class of metal-complexing functional groups did approach closely to 1.0 mol Ca^{2+}/ mol K/H fulvate (Sposito et al., 1978a). Thus, it would appear quite likely that some of the Cu^{2+} complexes with K/H fulvate involve bidendate sites.

The values of log ${}^{c}\bar{K}_1$ at each fulvate concentration are not significantly different: log ${}^{c}\bar{K}_1 = 2.11 \pm 0.02$ for the higher concentration and log ${}^{c}\bar{K}_1 = 2.06 \pm 0.09$ at the lower concentration. As was the case for proton complexation by K/H fulvate (Sposito et al., 1977), the difference between the formation functions in Fig. 20 and 21 can be accounted for simply by differences in the number of complexing sites per mole of fulvate.

Since virtually every previous investigation of Cu(II) complexation by fulvic acid has been carried out in either NO_3 or Cl background ionic media, it is not possible to compare the values of log ${}^{c}K_1$ and log ${}^{c}K_2$ determined in this study with other log stability constants for Cu fulvates (Gamble et al., 1970; Stevenson et al., 1973; Cheam, 1973; Cheam and Gamble, 1974; Buffle et al., 1977; Bresnahan et al., 1978). Moreover, in all but the last-mentioned of these investigations, overall conditional stability constants were measured instead of conditional stability constants related to complexation by specific classes of functional groups. Bresnahan et al. (1978) carried out a Scatchard plot analysis of their formation functions for Cu complexation in a NO_3 medium, but there is evidence that they did this incorrectly, since they state $n'_{Cu} = n_{Cu} - n_1$ (in the notation of this report) instead of the correct definition given by Scatchard et al. (1957). Mantoura and Riley (1975) have presented conditional stability constants for Cu(II) complexes with fulvic acid that are based on Scatchard plot analyses, but these data, unfortunately, pertain to a pH value of 8.0 instead of 5.0. Lastly, Manning and Ramamoorthy (1973) have studied Cu^{2+} complexes with fulvic acid in 0.1 M $NaClO_4$, but report only the overall thermodynamic stability constant. Therefore, no direct comparison between their data and those in Table 46 is possible. It should be added that in none of the investigations discussed here was the total fulvate concentration maintained constant.

SECTION 3

INCUBATION OF SEWAGE SLUDGE WITH SOILS

3.1. STUDIES WITH ONTARIO SLUDGE

Bradford et al. (1975) reported that sludge from the Ontario treatment plant had high concentrations of trace metals. Lund et al. (1976) found elevated concentrations of trace metals in soils beneath sludge drying beds at Ontario. Because of these findings we selected the Ontario sludge to use in laboratory incubation experiments to determine the effect of incubation water content, sludge application rate, time and sample preparation on the extractibility of selected trace metals from three sludge amended soils by three extractants.

Experimental

Materials

The treatments imposed in the incubation portion of this experiment made up a 2x3x5 factorial with two water contents (equivalent to 1/3 bar and saturation), three soils (Baywood-acid; Delhi-neutral; Calhi-calcareous) and five application rates (equivalent to 0, 5, 20, 50 and 100 metric T/ha). Each combination consisted of adding an appropriate amount of Ontario sludge to 450 g of soil in a plastic food container. The appropriate amount of water was added and the containers were covered and placed in a constant temperature room (25°C). Periodically, water was added during the incubation period to maintain the desired water content.

Extraction

After predetermined periods of incubation (1, 2, 3, 4, 6, 10, 14, 18, 22, 26, 32, 28, 45, and 52 weeks), containers representing all treatments were removed from the incubation room. The sludge-amended soils were extracted with 4 N HNO_3, 0.5 M DTPA, 1 N HOAc, and water (saturation extracts) and the concentrations of Cd, Cu, Ni and Zn in the extracts

were determined by atomic absorption spectrophotometry. As an additional treatment, the samples were extracted as taken from the incubation container (wet) or air-dried for one week prior to extraction (dry).

Statistical analysis

Analyses of variance were run on all data. Where significant main effects were found Duncan's Multiple Range test was carried out for mean separation. All significant differences reported in this Chapter are at the 1% level.

Recovery of Sludge-added Metals by Various Extractants

The emphasis of this study was to determine the degree to which sludge-added metals could be recovered by various extractants. This information will aid in interpreting future analyses of sludge-amended soils. In order to assess the recovery of only sludge-added metals, the metals contributed by the soil (0 mT/ha) were subtracted from all reported data and the recovery is reported as a percentage of the added metals. The data are presented first relative to extractants and then the treatment effects are discussed.

HNO_3

It was assumed prior to the experiment that the 4 N HNO_3 would extract all added metals and as such the relative recovery would not change with time. Therefore, the HNO_3 extraction was only carried out at 1, 2, and 3 weeks. The mean recovery by HNO_3 of added trace metals was 81% and ranged from 76% for Cu to 86% for Cd (Table 47). The less than 100% recovery indicates that 4 N HNO_3 was not completely effective in removing all the added metals. During incubation the metals must have been converted to forms resistant to extraction by HNO_3.

DTPA

DTPA extractable metals are often considered to indicate plant available metals. The mean recovery by DTPA added metals was approximately one-half of that by HNO_3, 42% (Table 47). If DTPA extractable metals are correlated with plant uptake, approximately one-half of the sludge added metals would be available to plants over a time period similar to that covered by this experiment. The recovery of metals by DTPA varied from 36% for Cu to 46% for Ni. Recovery of Cu was significantly lower than for the other three metals.

TABLE 47. RECOVERY OF ADDED TRACE METALS FROM SLUDGE-AMENDED SOILS BY FOUR EXTRACTANTS AS AFFECTED BY VARIOUS TREATMENT FACTORS.

Factor	Extractant Recovery		
	HNO_3	DTPA	HOAC
	---------- % ----------		
Incubation Water Content			
1/3 bar	79b*	48a	58a
Saturation	84a	37b	54b
Preparation Technique			
Wet	87a	41b	58a
Air-dried	76b	43a	53b
Application Rate			
5 T/ha	81a	45a	55a
20	80a	42b	56a
50	83a	41b	56a
100	82a	41b	56a
Soil			
Baywood	84a	41b	48c
Delhi	73b	39c	57b
Calhi	87a	46a	62a
Trace Elements			
Cu	76c	36c	16d
Ni	83ab	46a	70b
Zn	80bc	45a	74a
Cd	86a	43b	63c
Incubation Time			
1 week	82a	42b	55ab
2	84a	43b	57ab
3	79b	47a	57ab
4	--	43b	57ab
6	--	42bc	54b
10	--	41bc	55ab
22	--	41bc	55ab
26	--	41bc	55ab
38	--	42bc	59a
52	--	39c	55ab

* Values within any treatment factor for each extraction not followed by the same letter are significantly different at the 1% level.

HOAc

The mean recovery of added metals by HOAc was 55% and ranged from 16% for Cu to 74% for Zn (Table 47). The variation in recovery between metals was much greater for HOAc than for HNO_3 and DTPA. Until this variation can be shown to be meaningful it would appear that HNO_3 and DTPA would be more useful extractants as the recoveries from metal to metal were more uniform.

Water

If metals move in soil profiles, the soil solution is likely the transporting medium. Also soluble metals represent the metal more likely available for plant uptake. Therefore, concentrations of trace metals in saturation extracts were determined to assess the potential for movement, as well as to determine how the various treatments affect the pool of metals that may be available for plant uptake. The amounts of metals extracted by water were very low and it would be meaningless to express them as a percentage of the added, therefore, all saturation extractable metals were expressed as concentrations in the saturation extracts (Table 48). Because of this, it is not possible to determine a meaningful overall mean. Presenting the data for saturation extracts as concentrations allows the rate of application to become an important variable. For the 100 mT/ha rate the mean concentrations of Cu, Ni, Zn and Cd in the saturation extracts were 0.34, 25.07, 3.66, and 0.11 ug/ml, respectively. These concentrations were affected by many of the treatments as discussed later.

Recovery of Added Metals as Affected by Treatments

The main effects of treatment on metal recovery or concentrations are given in Tables 47 and 48. These data are discussed in the following sections along with more detailed data on some interactions.

Time

Extractions with HNO_3 were only carried out for the first three weeks of the study. The recovery was significantly lower at the third week than the first and second weeks (Table 47). It is not possible to determine if this was the start of a downward trend or just a chance occurrence. Studies of recovery of added metals by HNO_3 will have to be carried out over a longer period to determine if this apparent decline with time is meaningful.

No significant trends with time were found for recovery of added metals by DTPA or HOAc extractions (Table 47). Significant differ-

TABLE 48. MAIN EFFECTS OF TREATMENT ON CONCENTRATIONS OF FOUR TRACE METALS IN SATURATION EXTRACT OF SOIL AMENDED WITH SLUDGE AT FOUR RATES.†

Factor	Level	Cu 5	Cu 20	Cu 50	Cu 100	Ni 5	Ni 20	Ni 50	Ni 100	Zn 5	Zn 20	Zn 50	Zn 100	Ni 5	Ni 20	Ni 50	Ni 100
Incubation water content	1/3 bar	.03a	.10a	.22a	.44a	.55a	5.72a	16.36a	31.99a	.32a	2.28a	3.26a	3.54a	.01a	.04a	.09a	.13a
	Sat.	.03b	.05b	.10b	.23b	.22b	.90b	5.23b	18.16b	.07b	0.13b	1.80b	3.78a	.00b	.01b	.03b	.09b
Sample prep.	Wet	.02b	.06b	.12b	.25b	.38a	3.17a	10.42a	25.31a	.20a	1.19a	2.59a	3.89a	.01a	.02a	.05a	.11a
	Air-dried	.04a	.09a	.19a	.42a	.40a	3.45a	11.17a	24.84a	.19a	1.23a	2.47a	3.43a	.01a	.02a	.06a	.11a
Soil	Baywood	.02b	.06b	.18a	.31b	.77a	5.60a	15.72a	27.59a	.51a	2.89a	5.70a	7.07a	.00a	.02a	.08a	.12a
	Delhi	.04a	.10a	.15b	.33ab	.18b	3.37b	11.18b	20.86b	.04b	.66b	1.64b	2.23b	.01b	.03a	.07a	.10b
	Calhi	.03a	.07b	.13b	.37a	.22b	.96c	5.48c	26.76a	.04b	.07b	.25c	1.68b	.01a	.01b	.04b	.10b
Time	1	.03a	.06de	.13bc	.44a	.28a	2.11cd	5.60e	12.02d	.09b	.39c	.32e	.39d	.00a	.01d	.02e	.02e
	2	.03a	.06de	.13bc	.39ab	.28a	1.86d	5.56e	10.25d	.09b	.29c	.38e	.48d	.00a	.01d	.02e	.03de
	3	.03a	.05e	.11c	.32ab	.26a	1.71d	5.87e	11.88d	.08b	.26c	.37e	.61d	.00a	.01d	.02e	.04de
	4	.03a	.06de	.13c	.33ab	.26a	1.72d	6.50de	13.28d	.07b	.26c	.46e	.68d	.01a	.01cd	.03e	.04de
	6	.03a	.06de	.12c	.35ab	.30a	1.77d	6.42de	15.00d	.12ab	.30c	.48e	1.09d	.00a	.01cd	.03e	.06de
	10	.03a	.06cde	.12c	.27b	.35a	1.85d	7.33de	17.49d	.13ab	.40c	.84de	1.40d	.01a	.01cd	.04cde	.07d
	14	.03a	.07bcde	.15abc	.27b	.38a	2.43cd	10.65cde	26.18c	.17ab	.68bc	2.34cde	3.06cd	.01a	.02bcd	.06bcd	.11c
	18	.03a	.07abcde	.15abc	.28b	.42a	3.03bcd	11.36bcde	28.18bc	.20ab	.92bc	2.80bcde	4.04bcd	.00a	.02bcd	.07abc	.12c
	22	.03a	.07abcde	.16abc	.29b	.43a	3.70abcd	12.64abcd	28.88bc	.21ab	1.23abc	3.15bcde	4.11bcd	.01a	.03abc	.08ab	.13bc
	26	.03a	.08abcd	.18ab	.32ab	.45a	4.69abc	14.35abc	37.75a	.27ab	1.90abc	3.70abcd	6.53abc	.01a	.03ab	.08ab	.17a
	32	.03a	.09abc	.19a	.34ab	.47a	5.13ab	13.92abc	36.55ab	.28ab	2.36ab	3.74abcd	6.20abc	.01a	.04a	.09ab	.18a
	38	.03a	.10ab	.20a	.36ab	.51a	5.09ab	15.82abc	38.23a	.30ab	2.34ab	4.95abc	7.03ab	.01a	.03a	.09ab	.18a
	45	.03a	.10a	.21a	.39ab	.52a	5.54ab	17.10ab	39.79a	.34a	2.76a	5.58ab	9.68a	.01a	.04a	.10a	.19a
	52	.03a	.10a	.21a	.37ab	.53a	5.75a	17.98a	35.53ab	.36a	2.83a	6.33a	5.94bc	.01a	.04a	.10a	.16ab

† Values within any rate column for each factor followed by the same letter are not significantly different at the 1% level.

ences occurred but they appeared to be random and recoveries did not increase or decrease with time.

In all cases except Cu at 5 T and 100 T, and Ni at 5 T the concentrations of metals in saturation extracts increased with time (Table 48). During incubation the organic fraction of the sludge would decompose (see subsection 3.3) and one would expect metals to be released. Trace metals could be extracted to some degree with water and this accounts for the increase saturation extract concentrations with time.

Water content

Water contents equivalent to contents at 1/3 bar and saturation were maintained during the incubation period. The incubation water content had a significant effect on recovery by HNO_3. The recovery was significantly greater for samples incubated at saturation as compared to 1/3 bar (Table 47). However, when these data are broken down by metal and soil (Table 49), the only combination that had a significantly greater recovery for saturated than 1/3 bar samples was Ni and Delhi. Generally, the recovery was greater from saturated samples but the differences were significant in only the one case.

For DPTA extractable metals the effect of incubation water content was reversed from that found with HNO_3. Significantly less added metals was recovered from the saturated samples than from the 1/3 bar samples (Table 47). When broken down by metal and soil (Table 49), significant reductions in recovery occurred for 10 of the 12 cases. This would indicate that under anaerobic incubation the metals were converted to forms not extractable with DTPA. Perhaps sulfide forms were developed as many of the samples incubated at saturation turned very dark after a few weeks incubation.

The recovery of metals by HOAc was also reduced by saturated incubation (Table 47). For 6 of the 12 cases significantly less metal was recovered from the saturated samples (Table 49). No significant differences were found for the other six cases. Overall the recovery by HOAc was intermediate between that of HNO_3 and that of DTPA. It would appear that the intermediate acidity of HOAc contributed to this result. The exception was for copper where the recovery percentages were much lower for HOAc than for either DTPA or HNO_3. This would indicate a form of the copper that was not extractable by the weak acid. Based on other researchers' work, it is likely that the copper was in an organic form.

Metal concentrations in saturation extracts of soils incubated at saturation were significantly lower than those in extracts from 1/3 bar incubated soils (Table 48 and Table 50). Possible explanations for this are (1) reduced decomposition of organic fraction under anaerobic conditions and thus reduced release of metals from the organic fraction

TABLE 49. RECOVERY OF ADDED TRACE METALS FROM THREE SLUDGE-AMENDED SOILS BY THREE EXTRACTANTS AS AFFECTED BY INCUBATION WATER CONTENT.

Extractant	Water Content	Metal			
		Cu	Ni	Zn	Cd
		%			
		Baywood			
HNO_3	1/3 bar	77a†	86a	83a	90a
	Saturated	79a	87a	83a	87a
DTPA	1/3 bar	41a	58a	55a	45a
	Saturated	28b	40b	34b	28b
HOAc	1/3 bar	17a	70a	70a	43a
	Saturated	11b	66b	69a	40a
		Delhi			
HNO_3	1/3 bar	63a	71b	67a	72a
	Saturated	70a	82a	76a	83a
DTPA	1/3 bar	39a	50a	47a	50a
	Saturated	25b	28b	36b	37b
HOAc	1/3 bar	22a	68a	73a	72a
	Saturated	17b	68a	72a	66a
		Calhi			
HNO_3	1/3 bar	81a	82a	78a	94a
	Saturated	85a	90a	91a	98a
DTPA	1/3 bar	42a	46b	46b	52a
	Saturated	39b	52a	50a	43b
HOAc	1/3 bar	16a	76a	78a	85a
	Saturated	13b	71b	83a	73b

† Values are means of 2 reps, 2 sample preparations, 4 rates and 3 times (HNO_3) or 10 times (DTPA or HOAc). Values in columns for each extractant and incubation water content not followed by the same letter are significantly different at the 1% level.

of the sludge, and (2) formation of less soluble forms of the metals under anaerobic conditions. Both of these processes likely occurred.

TABLE 50. CONCENTRATIONS OF FOUR TRACE METALS IN SATURATION EXTRACTS OF THREE SOILS AS AFFECTED BY INCUBATION WATER CONTENT AND SAMPLE PREPARATION.

Soil	Factor	Level	Metal			
			Cu	Ni	Zn	Cd
			µg/ml			
Baywood	Incubation water content	1/3 bar	0.19a†	14.61a	4.49a	0.06a
		Saturation	0.09b	10.23b	3.60a	0.05b
	Sample preparation	Wet	0.12b	12.48a	4.18a	0.06a
		Air-dried	0.17a	12.36a	3.91a	0.06a
Delhi	Incubation water content	Wet	0.20a	14.88a	1.86a	0.07a
		Air-dried	0.10b	2.92b	0.42b	0.02b
	Sample preparation	Wet	0.12b	9.09a	1.23a	0.05a
		Air-dried	0.19a	8.71a	1.06a	0.05a
Calhi	Incubation water content	Wet	0.20a	11.48a	0.70a	0.06a
		Air-dried	0.11b	5.24b	0.32b	0.02b
	Sample preparation	Wet	0.10b	7.88a	0.50a	0.04a
		Air-dried	0.21a	8.83a	0.52a	0.04a

†Values are means of 2 reps, 2 (either sample prep or water content), 4 rates and 14 times. Values in columns for each soil and factor not followed by the same letter are significantly different at the 1% level.

Rate

The rate of application generally did not affect the recovery of added metals by HNO_3, DTPA or HOAc (Table 47). Only for DTPA, the 5T/ha rate was significantly different from the other rates. Within the rates tested here, regardless of amount of metal added the same proportion was recoverable by these extractants. Therefore, in future incubation studies one rate may be adequate.

For saturation extracts there were significant differences between metal concentrations resulting from the various application rates (Table 51). The relationships between rates and metal concentrations were generally linear (Fig. 23). Again this would suggest that only the concentration changes with rate and not the relationship between concentration and rate.

Sample Preparation

Most investigators, when they do soil analysis, start with an air dry soil. After soils are sampled in the field or taken from greenhouse pots, they are air dried and crushed prior to analysis. Drying soils allows for changes in chemical forms of soil constituents. Therefore, alternative sample preparations were used to determine if air drying the sludge-amended soils would affect the extractability of the added metals. These treatments consisted of extracting the samples directly after removing the sample from the incubation container or extracting samples after they had air-dried in the laboratory for 1 week.

Air-drying significantly reduced the recovery of added metals by HNO_3 and HOAc (Table 47). When the results are broken down by metal and soil (Table 52), significant reductions were found for 7 of 12 cases for HNO_3 and HOAc. Significant increases on air drying were found in 2 of the 12 cases for DTPA. It appears that on air drying the metals were changed to a form that was less soluble in acid thus, the reduced recovery. The DTPA extractable metals did not appear to be affected. The forms of metals that exist in sludge-amended soils and the effect of form on extractability needs to be determined in future research.

The reduced recovery of metals after air-drying suggests that metal concentrations in acidic extracts obtained after air-drying samples would underestimate the amount present in the soil. Therefore, care must be taken when extrapolating these concentrations to field situations.

When using saturation extracts, air-drying the sludge-amended soils only affected the Cu concentrations (Table 48 and 50). The Cu concentration increased after air drying. A possible explanation is that on air drying the organic matter would oxidize to some extent. Copper is thought to be associated with organic matter to a greater extent than are the other metals. Thus, as the organic matter oxidized, copper complexed with the organic matter would be released.

Soil

The effects of soil on the recovery of metals by HNO_3, DTPA or HOAc tended to be confusing (Table 47). The only consistent result was that the recoveries were greater for the Calhi soil than for the Delhi

TABLE 51. CONCENTRATIONS OF FOUR TRACE METALS IN SATURATION EXTRACTS OF THREE SOILS AS AFFECTED BY SLUDGE APPLICATION RATE.

Application rate	Metal			
	Cu	Ni	Zn	Cd
T/ha	µg/ml			
	Baywood Soil			
5	0.02d†	0.77d	0.50c	0.002d
20	0.06c	5.60c	2.90b	0.024c
50	0.18b	15.72b	5.70a	0.075b
100	0.31a	27.60a	7.07a	0.124a
	Delhi Soil			
5	0.04d	0.18d	0.04d	0.006d
20	0.10c	3.37c	0.66c	0.029c
50	0.15b	11.18b	1.64b	0.066b
100	0.33a	20.86a	2.23a	0.097a
	Calhi Soil			
5	0.03c	0.22c	0.04c	0.008c
20	0.07c	0.96c	0.06c	0.015c
50	0.13b	5.48b	0.25b	0.037b
100	0.37a	26.76a	1.68a	0.098a

† Values are means of 2 reps, 2 sample preps, 2 incubation water contents, and 14 times. Values in columns for each soil not followed by the same letter are significantly different at the 1% level.

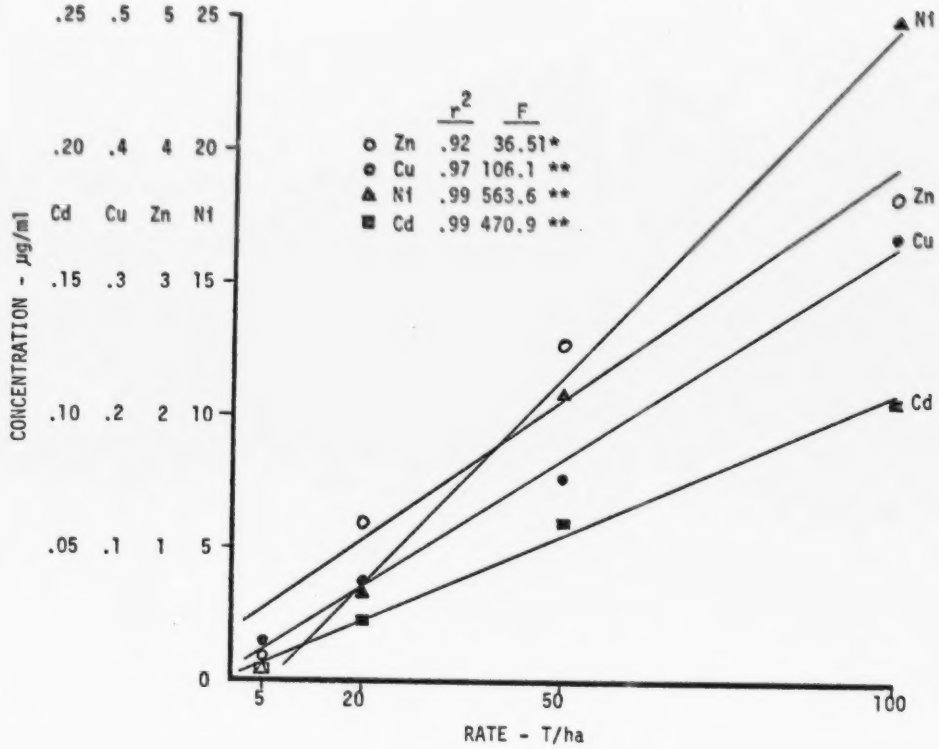

Fig. 23. Relationships between mean saturation extract metal concentration and rate for four metals.

TABLE 52. RECOVERY OF ADDED TRACE METALS FROM THREE SLUDGE-AMENDED SOILS BY THREE EXTRACTANTS AS AFFECTED BY SAMPLE PREPARATION.

Extractant	Sample Preparation	Metal			
		Cu	Ni	Zn	Cd
		%			
		Baywood			
HNO_3	Wet	85a†	90a	88a	89a
	Air-dried	72b	82a	79a	88a
DTPA	Wet	34a	49a	43a	35a
	Air-dried	35a	50a	46a	39a
HOAc	Wet	14a	70a	73a	46a
	Air-dried	13a	66b	66b	37b
		Delhi			
HNO_3	Wet	78a	82a	81a	87a
	Air-dried	55b	71b	62b	69b
DTPA	Wet	32a	39a	39b	40b
	Air-dried	33a	39a	44a	46a
HOAc	Wet	21a	71a	79a	73a
	Air-dried	18a	65b	67b	65b
		Calhi			
HNO_3	Wet	91a	91a	91a	98a
	Air-dried	76b	81b	78a	94a
DTPA	Wet	40a	50a	46a	46a
	Air-dried	40a	48a	50a	50a
HOAc	Wet	15a	73a	85a	81a
	Air-dried	14a	73a	76b	77a

†Values are means of 2 reps, 2 incubation water contents, 4 rates and 3 times (HNO_3) or 10 times (DTPA or HOAc). Values in columns for each extractant and sample preparations not followed by the same letter are significantly different at the 1% level.

or Baywood. This is likely because these extracting agents are strong compared to the soil acidity levels and extracted approximately the same relative amounts from each soil. This was especially true for HNO_3.

For the saturation extracts the effects of soil were much more evident especially for Ni and Zn. Extract from the acid soil, Baywood, had significantly greater metal concentrations than the neutral soil, Delhi, which was greater than the calcareous soil, Calhi (Table 48 and 50). This is in keeping with the concern over the greater availability and potential problems of metals when sludge is applied to acid soils. The metals are not "fixed" by soil constituents in this case and are "available" for uptake or movement.

3.2. STUDIES OF METAL EXTRACTABILITY WITH SEVEN SLUDGES

The previously discussed work demonstrated that for soils amended with Ontario sludge, metal extractability varied with time, water content, sample preparation, soil and extractant. However, these results were only for one sludge. In order to determine the effects of these treatments more fully, additional studies were conducted using seven sludges representing a range of characteristics.

Experimental

The same treatment variables were used as in the previous study except for rate and HOAc as an extractant. A constant rate of 100 T/ha was used because in the previous study, rate did not affect the recovery of metals by HNO_3 or DTPA.

Materials and design

The factors and levels used in this study were sludges (7, see Table 53), incubation water contents (1/3 bar and saturated), soils (Baywood, Delhi, and Calhi), sample preparation (wet and air-dried), times (7) and extractants (HNO_3, DTPA and saturation extracts). All treatments were replicated three times. Soil or sludge-soil mixtures (100 T sludge/ha) were prepared as described in Section 3.1. Periodically sample containers were removed from the constant temperature room.

Extractants

Wet and air-dried samples were extracted with 4N HNO_3, 0.5 M DTPA

TABLE 53. TOTAL METAL CONTENTS OF SOILS AND SLUDGES USED IN THE INCUBATION STUDY.

	Cd	Cu	Ni	Pb	Zn
	µg/g				
Soils					
Baywood	<0.13	2.75	22.5	1.13	11.8
Calhi	<0.13	4.65	5.5	1.13	22.0
Delhi	<0.13	9.97	10.1	4.41	40.7
Sludges					
Rialto	11.0	490	39	289	1490
LA Composted	34.0	670	260	1480	2050
Colton	10.5	835	499	6300	2560
Ontario	88.7	588	1880	378	2420
Escondido	198	1810	167	667	2920
LA Liquid	64.8	1120	448	1300	4200
Kokomo	1140	3350	540	511	24270

or water as saturation extracts at 2, 4, 10, 18, 26, 34, and 50 weeks after the beginning of the incubation period. The soil solution ratios and digestion or shaking times were as follows: HNO_3 - 2:25, 80°C, 16 hrs; DTPA - 10:20, 16 hrs; H_2O-saturation extracts, 2 hrs. The extracts were analyzed for Cd, Cu, Ni, Pb and Zn by atomic absorption spectrophotometry. Lead concentrations were below detection limits for all saturation extracts and thus no Pb-SE data are reported.

Speciation studies

Saturation extracts collected from some treatments after 50 weeks of incubation were analyzed extensively for cationic and anionic composition.

These data were input to GEOCHEM (see Section 1) as a means to determine speciation of the metals in the soil solutions.

Recovery of sludge-added metals by various extractants

Metal recovers for HNO_3 and DTPA extracts were expressed as percentages of sludge added metals. Concentrations of metals in the saturation extracts were reported where water was the extracting agent.

HNO_3

The recovery of metals by HNO_3 over the duration of the study was quite close to complete with a mean of 97% for all treatments (Table 54). There was a trend for decreased recovery with time as the recovery was significantly reduced at the later extractions for all five metals. Apparently the metals were being converted over time to forms that were less soluble in HNO_3. However, the reduced recovery was very small and does not detract from using HNO_3 extraction as a measure of added-metals present in sludge-amended soils.

DTPA

The recovery of added metals by DTPA was much less than that by HNO_3. The mean recovery was 38% (Table 54). For Cu and Ni, the recovery appeared to increase with time; whereas, the recovery tended to decrease for Cd, Zn and Pb. The mean recovery varied with sludge and with metal, however, the maximum mean variation was approximately 10%. Thus, it is difficult to generalize as to the expected recovery of added metals by DTPA.

Saturation Extracts

Recovery

The concentrations of Zn, Cu, Ni and Cd in saturation extracts are given in Tables 55 - 58. Because of the large effects of sludge and incubation water content, mean data are reported separately for these factors. Mean saturation extract concentrations for the various sludges varied greatly because of the differing amounts of added metals (Table 53). The fact that a sludge had a low amount of a certain metal did not always result in a low concentration of that metal in the saturation extract. For example, comparatively little Zn was added in the Rialto sludge but the mean Zn concentration in saturation extracts of Rialto sludge-amended soils was greater than three sludge treatments that resulted in greater Zn applications, LA composted, LA liquid and Kokomo.

TABLE 54. RECOVERY OF ADDED TRACE METALS FROM SLUDGE-AMENDED SOILS BY HNO_3 OR DTPA EXTRACTION AS AFFECTED BY VARIOUS TREATMENTS.

Factor	Level	Cu		Ni		Cd		Zn		Pb	
		HNO_3	DTPA	HNO_3	DTPA	HNO_3	DTPA	HNO_3	DTPA	HNO_3	DTPA
		-----%-----		-----%-----		-----%-----		-----%-----		-----%-----	
Sludge	Rialto	91z	27y	60z	32x	94yz	33z	96z	40x	93y	33y
	LA comp	92z	31x	91y	29y	92z	38y	97z	37y	85z	36w
	Colton	91z	26z	94y	52u	103x	38xy	95z	52v	93y	37v
	Ontario	103x	41v	108w	52u	109w	45w	103y	51v	103wx	34x
	Escondido	98y	34w	94y	43v	106wx	39x	102y	45w	100wx	34xy
	LA liquid	100y	44u	92y	40w	107wx	50v	95z	45w	104w	42u
	Kokomo	100y	40v	99x	7z	97y	50v	101y	34z	99x	24z
Soil	Baywood	95z	32z	85z	30z	103y	39z	98z	39z	95z	34y
	Delhi	98y	33y	95y	40y	101y	43y	99z	44y	97y	38z
	Calhi	97y	39x	93y	39y	99z	44y	98z	47x	98y	31x
Water Content	1/3 bar	98y	48y	91z	38y	102z	51y	99z	49y	96z	31z
	Saturation	95z	21z	91z	35z	100y	33z	98z	37z	97z	37y
Sample Prep	Wet	101y	29z	95y	35z	104y	34z	102y	37z	102y	31z
	Air-dried	92z	40y	88z	37y	98z	49y	95z	49y	91z	37y
Time	2	101x	30z	99w	36xy	103y	42y	101vw	44x	100xy	37w
	4	98xy	33y	94x	37w	100yz	42y	100vwx	45w	98xy	38w
	10	100x	39u	91xy	37w	107x	43xy	102v	46w	101x	35x
	18	93z	38v	91xy	35y	98z	43x	96yz	42yz	94z	32y
	26	96yz	33y	89yz	34z	101yz	42xy	98wxy	41z	97yz	31z
	34	94z	35w	87z	37wx	99yz	42y	97xyz	42y	93z	33y
	50	95z	34x	86z	37wx	98z	40z	95z	41z	94z	32yz

TABLE 55. CONCENTRATIONS OF Zn IN SATURATION EXTRACTS OF SLUDGE-AMENDED SOILS INCUBATED AT 1/3 BAR AND SATURATION AS AFFECTED BY VARIOUS TREATMENTS.

Incubation water content	Factor	Level	Sludge						
			Rialto	LA comp	Colton	Ontario	Escondido	LA liquid	Kokomo
			µg/ml						
1/3 Bar	Soils	Baywood	.94y	1.70y	3.61z	5.52x	1.83z	1.04y	.34z
		Delhi	2.21x	.21z	6.98y	2.17y	3.12y	1.42x	1.00y
		Calhi	.55z	.15z	2.90z	.94z	2.14z	.83z	.97y
	Samp Prep.	Wet	1.15z	.68z	4.22z	2.94z	2.14z	.75z	.69z
		Air-dried	1.31z	.69z	4.77z	2.82z	2.58y	1.44y	.85y
	Time	2	.32z	.36z	.56z	1.53z	.85z	.54z	.89x
		4	.55yz	.67y	1.73z	1.30z	1.43y	.53z	.80y
		10	.88xy	.59y	3.40y	1.37z	1.66xy	.73z	.75y
		18	1.12wx	.68y	4.85xy	1.45z	1.86xy	1.31y	.72yz
		26	1.42w	.69y	6.07wx	2.26z	2.27wx	1.26y	.76y
		34	2.03v	.94x	7.23w	4.31y	2.65w	1.43y	.80y
		50	2.30v	.87x	7.61w	7.93x	5.82v	1.86x	.66z
Saturation	Soil	Baywood	.30y	.10y	.49y	.38x	.44y	.34y	.70y
		Delhi	.09z	.03z	.11z	.13y	.13z	.19z	.35z
		Calhi	.11z	.04z	.18z	.05z	.11z	.15z	.72y
	Samp. Prep.	Wet	.12z	.03z	.15z	.08z	.09z	.06z	.62y
		Air-dried	.21y	.08y	.37y	.30y	.36y	.39y	.55z
	Time	2	.28x	.06yz	.19yz	.17yz	.23yz	.09z	1.25w
		4	.11yz	.03z	.13z	.26y	.19yz	.19z	1.01x
		10	.12yz	.04z	.21yz	.18yz	.22yz	.34y	.56y
		18	.22xy	.07yz	.32yz	.14z	.33y	.35y	.37z
		26	.17xyz	.07yz	.26yz	.21yz	.16z	.21z	.35z
		34	.17xyz	.09y	.41y	.23yz	.28yz	.21z	.32z
		50	.09z	.03z	.30yz	.14z	.17z	.19z	.26z

TABLE 56. CONCENTRATIONS OF Cd IN SATURATION EXTRACTS OF SLUDGE-AMENDED SOILS INCUBATED AT 1/3 BAR AND SATURATION AS AFFECTED BY VARIOUS TREATMENTS.

Incubation water content	Factor	Level	Sludge						
			Rialto	LA comp	Colton	Ontario	Escondido	LA liquid	Kokomo
			µg/ml						
1/3 Bar	Soils	Baywood	.02z	.04x	.02z	.11y	.10z	.05z	.15z
		Delhi	.04y	.03y	.05y	.11y	.23x	.09x	.17y
		Calhi	.04y	.02z	.06x	.09z	.18y	.07y	.24x
	Samp Prep.	Wet	.03z	.03z	.04z	.10z	.15z	.06z	.17z
		Air-dried	.03z	.03y	.04z	.11z	.19y	.08y	.20y
	Time	2	.01z	.02z	.02z	.06z	.08z	.05z	.19x
		4	.02z	.02z	.02z	.06z	.11z	.05z	.17z
		10	.03y	.03xy	.04y	.08y	.15y	.07y	.17z
		18	.04x	.03x	.05xy	.09y	.18xy	.08x	.18y
		26	.04x	.04w	.06x	.10y	.21x	.08wx	.19xy
		34	.04x	.03y	.06x	.12x	.20x	.08wx	.20w
		50	.05x	.03xy	.06x	.20w	.27w	.09w	.19xy
Saturation	Soil	Baywood	.01y	.01z	.01z	.01yz	.02z	.02z	.11y
		Delhi	.03x	.01y	.01z	.01z	.02y	.02z	.06z
		Calhi	.01z	.01yz	.01z	.01y	.02z	.01z	.16x
	Samp. Prep.	Wet	.01z	.01z	.01z	.01z	.01z	.01z	.09z
		Air-dried	.02y	.01y	.01z	.02y	.02y	.02y	.13y
	Time	2	.01y	.01x	.01yz	.01z	.02y	.01z	.25v
		4	.00z	.01y	.00z	.01z	.02y	.01z	.19w
		10	.01w	.01w	.01xy	.02x	.03x	.02y	.12x
		18	.01x	.01v	.02x	.01y	.02y	.02y	.07y
		26	.01wx	.01wx	.01xyz	.02xy	.02y	.02y	.06y
		34	.05v	.01z	.02x	.02y	.02y	.02y	.06y
		50	.00y	.01yz	.01xyz	.01z	.00z	.01z	.03z

TABLE 57. CONCENTRATIONS OF Cu IN SATURATION EXTRACTS OF SOILS AMENDED WITH SEWAGE SLUDGE INCUBATED AT 1/3 BAR AND SATURATION AS AFFECTED BY VARIOUS TREATMENTS.

Incubation water content	Factor	Level	Sludge						
			Rialto	LA comp	Colton	Ontario	Escondido	LA liquid	Kokomo
			µg/ml						
1/3 Bar	Soils	Baywood	.49x	.15y	.78y	.34z	1.52y	.65y	.24y
		Delhi	.20z	.11z	.46z	.32z	.81z	.50z	.22yz
		Calhi	.27y	.14y	.66y	.41y	1.05z	1.14x	.21z
	Samp Prep.	Wet	.26z	.12z	.51z	.30z	.93z	.54z	.15z
		Air-dried	.38y	.16y	.75y	.41y	1.32y	.98y	.30y
	Time	2	.30yz	.13z	.60y	.38x	2.07x	1.38v	.20z
		4	.26z	.13z	.39z	.36xy	1.34y	1.12w	.19z
		10	.23z	.14z	.36z	.32yz	.86yz	.77x	.19z
		18	.25z	.14z	.42yz	.29z	.96yz	.65y	.32x
		26	.31yz	.14z	.59y	.30z	.67z	.52z	.25y
		34	.51x	.14z	.87x	.36xy	.86yz	.46z	.20z
		50	.38y	.14z	1.21w	.49w	1.13yz	.43z	.22yz
Saturation	Soil	Baywood	.06y	.04y	.05z	.07x	.10yz	.07z	.14y
		Delhi	.03z	.01z	.04z	.11y	.08z	.07z	.09z
		Calhi	.06y	.04y	.09y	.23x	.12y	.10z	.14y
	Samp. Prep.	Wet	.01z	.00z	.03z	.01z	.02z	.01z	.03z
		Air-dried	.08y	.06y	.10y	.26y	.18y	.15y	.21y
	Time	2	.04z	.02z	.02z	.13yz	.07yz	.01z	.23v
		4	.02z	.02z	.02z	.12yz	.07yz	.05yz	.18w
		10	.04z	.02z	.04yz	.07z	.08yz	.09xy	.14x
		18	.09y	.06y	.08xy	.27x	.21x	.14x	.11xy
		26	.08y	.03z	.08xy	.18y	.11y	.12x	.09yz
		34	.05z	.03z	.10x	.12yz	.11y	.09xy	.05z
		50	.02z	.03z	.07xyz	.08z	.06z	.07y	.07z

TABLE 58. CONCENTRATIONS OF Ni IN SATURATION EXTRACTS OF SLUDGE-AMENDED SOILS INCUBATED AT 1/3 BAR AND SATURATION AS AFFECTED BY VARIOUS TREATMENTS.

Incubation water content	Factor	Level	Sludge						
			Rialto	LA comp	Colton	Ontario	Escondido	LA liquid	Kokomo
			µg/ml						
1/3 Bar	Soils	Baywood	.29z	.40x	2.18z	9.26z	.61z	.58z	.09z
		Delhi	.30z	.21z	2.89y	8.67z	.77y	.81y	.12y
		Calhi	.31z	.26y	2.75y	8.55z	.69yz	.98x	.12y
	Samp Prep.	Wet	.29z	.28z	2.33z	8.50z	.65z	.71z	.10z
		Air-dried	.31z	.30y	2.89y	9.16y	.73y	.87y	.11y
	Time	2	.38w	.32x	1.71z	6.75z	.82wx	.81xy	.10y
		4	.28y	.31xy	1.55z	7.32z	.58yz	.84wx	.18x
		10	.23z	.28yz	2.01yz	7.26z	.52z	.74yz	.10y
		18	.28y	.28yz	2.44y	6.90z	.62yz	.81xy	.11y
		26	.31xy	.30xy	2.99x	7.91z	.71xy	.75yz	.10y
		34	.34wx	.29xy	3.49w	10.00y	.68y	.71z	.08z
		50	.28y	.26z	4.07v	15.66x	.89w	.88w	.08z
Saturation	Soil	Baywood	.27y	.21y	.68y	2.81y	.33x	.60z	.16y
		Delhi	.21z	.22y	.52z	1.69z	.22z	.62z	.14y
		Calhi	.29y	.15z	1.01x	2.67y	.28y	.78y	.18x
	Samp. Prep.	Wet	.23z	.12z	.45z	1.45z	.22z	.50z	.17y
		Air-dried	.28y	.27y	1.03y	3.33y	.33y	.83y	.14z
	Time	2	.34x	.27w	.85y	3.11w	.35u	.83x	.22w
		4	.27y	.21x	.69yz	2.64x	.30vw	.77xy	.28v
		10	.27y	.20x	.50z	2.34y	.28wx	.72y	.16x
		18	.26y	.18xy	1.12x	2.80x	.32v	.61z	.13y
		26	.27y	.15z	.78y	2.26y	.26xy	.58z	.10z
		34	.21z	.16yz	.74y	1.88z	.24y	.58z	.10z
		50	.19z	.16yz	.48z	1.69z	.21z	.58z	.11z

The trends with time were also very confusing and in many cases made it apparent that concentrations averaged over time would be meaningless. These data would indicate that when growing plants in sludge amended soils saturate extract concentrations of metals at the start or end of an experiment may not accurately represent the metals available for plant uptake during the study.

Speciation

Saturation extracts of sludge amended soils incubated for 50 weeks were analyzed for cationic and anionic composition. These data were analyzed using GEOCHEM to predict the forms of the trace metals in the soil solutions. The predicted forms were summarized and are reported as free ionic, inorganically complexed and organically complexed (Tables 59 through 62.

Cadmium was found to be present in the extracts principally as free ionic forms with smaller percentages present as organically-complexed (Table 59). For samples incubated at 1/3 bar, the only real exception to this was for the LA liquid sludge where inorganically-complexed Cd accounted for the greatest proportion of Cd in the extracts. Incubation at saturation resulted in a shift in form from free ionic to organically-complexed. This happened in every case where Cd was detectable in the saturation extracts of the samples incubated at saturation.

Most of the Cu existed as organically-complexed Table 60. In a few cases (Baywood-Ontario, Delhi-Rialto, Delhi-Colton and Delhi-Escondido) there was a sizeable percentage of Cu existing as free ionic. These cases appeared to be random and are not readily explainable. The Cu concentrations in many of the saturation extracts from saturated samples were below the detection limit. However, the data that did exist suggest that the conversion of Cu to organically-complexed forms was essentially complete after incubation in saturated conditions.

Free ionic forms accounted for the majority of Ni present in saturation extracts of samples incubated at 1/3 bar (Table 61). Small amounts of organically-complexed Ni were present with intermediate amounts of inorganically-complexed Ni. Incubation at saturation resulted in a shift away from the free ionic form to organically-complexed N which left very little Ni as free ionic. This shift in Ni form was much more dramatic than for Cd.

For samples incubated at 1/3 bar, the results for Zn were similar to those of Cd and Ni, free ionic accounted for the greatest portion of the Zn with small amounts present as organically-complexed (Table 62). Incubation at saturation, however, resulted in a different shift. For Zn, the shift was to inorganically-complexed forms.

The results of the GEOCHEM analyses showed that Cu existed principally as organically-complexed forms, whereas; Zn, Cd and Ni existed

TABLE 59. SPECIATION OF Cd IN SATURATION EXTRACTS OF SLUDGE-AMENDED SOILS AFTER 50 WEEKS OF INCUBATION. F = free ionic, I = inorganically complexed, O = organically complexed.

Incubation Water Content	Soil	Species	Sludge						
			Rialto	LA Comp	Colton	Ontario	Escondido	LA Liquid	Kokomo
1/3 bar	Baywood	F	58.6	68.1	52.0	70.9	54.4	37.6	73.3
		I	22.0	29.8	23.5	26.0	36.5	58.0	23.1
		O	19.1	2.0	24.3	3.1	9.0	4.3	3.5
	Delhi	F	75.2	72.0	74.0	71.0	67.8	42.9	79.7
		I	20.6	26.0	19.7	22.2	29.5	54.9	15.9
		O	4.2	1.7	6.2	6.6	3.0	2.0	4.2
	Calhi	F	75.7	71.4	70.2	68.4	64.2	41.2	72.2
		I	19.9	25.9	18.9	21.0	31.7	53.5	23.4
		O	4.1	2.6	10.7	10.3	3.9	5.3	4.4
Saturation	Baywood	F	--†	41.8	--	24.8	41.7	24.8	61.1
		I	--	14.8	--	6.2	23.4	60.0	29.3
		O	--	43.2	--	69.0	34.8	14.9	9.6
	Delhi	F	33.3	--	33.4	30.3	42.4	31.9	--
		I	34.9	--	40.5	30.3	26.4	43.1	--
		O	31.7	--	25.6	39.2	31.1	25.0	--
	Calhi	F	39.1	--	--	--	--	26.3	52.7
		I	17.0	--	--	--	--	58.0	31.8
		O	40.9	--	--	--	--	15.6	15.4

† Indicates metal concentration below detection limit.

TABLE 60. SPECIATION OF Cu IN SATURATION EXTRACTS OF SLUDGE-AMENDED SOILS AFTER 50 WEEKS OF INCUBATION. F = free ionic, I = inorganically complexed, O = organically complexed.

Incubation Water Content	Soil	Species	Sludge						
			Rialto	LA Comp	Colton	Ontario	Escondido	LA Liquid	Kokomo
1/3 bar	Baywood	F	0.8	2.0	0.9	45.5	4.8	0.9	0.7
		I	0.9	0.7	1.0	15.5	3.2	1.4	1.6
		O	98.1	97.0	98.0	39.0	91.9	97.6	97.7
	Delhi	F	28.0	1.1	21.2	6.1	23.7	2.4	0.6
		I	6.5	0.9	5.2	2.6	5.5	1.9	1.7
		O	65.0	97.9	73.5	91.3	70.8	95.5	97.5
	Calhi	F	3.3	0.3	1.9	0.8	3.6	0.2	0.5
		I	2.8	0.2	2.4	1.8	3.1	0.9	1.4
		O	93.7	99.3	95.8	97.3	93.1	98.7	98.0
Saturation	Baywood	F	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		I	0.1	0.2	0.2	0.0	0.2	0.5	0.7
		O	99.9	99.9	100.0	100.0	99.8	99.5	99.2
	Delhi	F	-- †	--	--	--	--	--	--
		I	--	--	--	--	--	--	--
		O	--	--	--	--	--	--	--
	Calhi	F	--	--	--	0.0	--	0.0	--
		I	--	--	--	0.1	--	0.3	--
		O	--	--	--	99.8	--	99.6	--

† Indicates metal concentration below detection limit.

TABLE 61. SPECIATION OF Ni IN SATURATION EXTRACTS OF SLUDGE-AMENDED SOILS AFTER 50 WEEKS OF INCUBATION. F = free ionic, I = inorganically complexed, O = organically complexed.

Incubation Water Content	Soil	Species	Sludge						
			Rialto	LA Comp	Colton	Ontario	Escondido	LA Liquid	Kokomo
1/3 bar	Baywood	F	58.8	73.8	51.9	75.2	63.4	61.8	67.3
		I	20.0	23.0	21.4	20.7	25.1	29.2	27.0
		O	21.2	2.9	26.7	3.9	11.3	8.8	5.6
	Delhi	F	79.2	75.1	77.6	74.8	81.2	75.0	70.8
		I	16.1	21.4	15.3	18.3	14.9	20.9	22.8
		O	4.6	3.4	6.9	6.7	3.7	4.0	6.3
	Calhi	F	77.4	72.1	70.9	66.2	75.9	58.3	65.6
		I	18.2	19.0	18.4	22.5	19.3	27.8	27.8
		O	4.5	8.3	10.5	11.2	4.7	13.7	6.7
Saturation	Baywood	F	10.0	--†	11.6	5.4	18.1	1.7	8.9
		I	18.5	--	29.5	12.4	26.3	66.1	68.1
		O	70.8	--	58.8	82.2	55.4	32.1	22.7
	Delhi	F	1.4	1.9	1.3	1.2	2.3	1.5	1.3
		I	59.3	70.2	63.9	44.1	52.1	68.1	56.3
		O	39.1	27.7	34.6	54.4	45.3	30.1	42.2
	Calhi	F	2.3	--	3.0	1.7	4.3	2.7	4.9
		I	36.6	--	72.6	36.1	45.3	56.0	72.3
		O	60.9	--	24.1	61.9	50.3	40.9	22.7

†Indicates metal concentration below detection limit.

TABLE 62. SPECIATION OF Zn IN SATURATION EXTRACTS OF SLUDGE-AMENDED SOILS AFTER 50 WEEKS OF INCUBATION. F = free ionic, I = inorganically complexed, O = organically complexed.

Incubation Water Content	Soil	Species	Sludge						
			Rialto	LA Comp	Colton	Ontario	Escondido	LA Liquid	Kokomo
1/3 bar	Baywood	F	69.3	71.5	64.3	74.4	66.2	64.1	71.1
		I	26.0	27.7	29.8	24.9	31.7	34.3	28.0
		O	4.5	0.4	5.7	0.6	2.1	1.4	0.7
	Delhi	F	80.2	75.0	80.4	76.4	81.8	75.3	77.7
		I	18.7	24.5	18.0	22.0	17.3	20.1	21.2
		O	0.9	0.4	1.5	1.6	0.7	0.8	0.9
	Calhi	F	79.3	75.8	77.2	73.6	77.4	69.8	69.9
		I	19.6	23.2	19.6	22.8	21.5	27.9	29.1
		O	1.0	0.8	2.9	2.6	1.1	2.3	0.9
Saturation	Baywood	F	46.3	34.6	43.8	42.2	54.3	11.1	30.6
		I	41.5	58.7	48.0	41.4	37.6	85.4	67.3
		O	12.1	6.5	8.0	16.3	7.9	3.4	1.9
	Delhi	F	10.6	-- †	9.8	11.6	16.6	9.1	--
		I	84.3	--	86.0	80.4	78.5	87.1	--
		O	5.0	--	4.0	7.9	4.8	3.6	--
	Calhi	F	20.0	16.3	14.7	16.1	25.2	17.3	20.0
		I	74.5	80.9	81.8	75.2	69.4	77.1	77.5
		O	5.4	2.7	3.2	8.5	5.3	5.6	2.4

† Indicates metal concentration below detection limit.

mainly as free ionic forms in samples incubated at 1/3 bar. Incubation under saturated conditions resulted in a change of forms from free ionic to organically-complexed for Cd and Ni and to inorganically-complexed for Zn.

Effect of various factors on extractability of metals

Sludge

Sludges, added at a constant rate, add differing amounts of metals because of the differing concentrations of metals in the sludges (Table 53). This results in differing amounts of metals being available for plant uptake, movement or extraction. The varying concentrations of metals present in saturation extracts of sludge-amended soils in this study were, therefore, to be expected. However, the relationship between metal added and concentrations in saturation extracts was generally not predictable. Even when the extractability was expressed as a percentage of the added, as it was for HNO_3 and DTPA extractions, the sludges were found to have a significant effect. This supports the conclusion that sludges are highly variable and the fact that they contain the same amount of metals does not indicate how these metals will react in the soil system.

Time

Time had definite effects on the extractability of metals from sludge-amended soils in this study. Total metals as measured by HNO_3 extraction decreased with time suggesting that the metals were being converted to forms not extractable with HNO_3 (Table 54). This decrease was small, however, and does not eliminate the use of HNO_3 extractable metals as a measure of total metals added in sludges. The variability with time was greater for DTPA extracts and trends with time were not apparent (Table 54). These results indicate that DTPA extractions can be made anytime during the first year after addition of sludge to soil and continuous monitoring by DTPA extractions would not be worthwhile.

Concentrations of metals in saturation extracts varied with time (Tables 55-58). However, the trends with time were not uniform, some increased, some decreased and some did both over the 50 week study. There were also significant interactions between time and soil, sludge, and incubation water content. For example, consider Cd (Table 56). The concentrations of Cd in saturation extracts increased with time for all sludges incubated at 1/3 bar except Kokomo which remained generally constant. For saturated samples, the Cd concentrations remained the same with time except for the Kokomo sludge where they decreased. The Kokomo sludge was the only sludge not from southern California and appears to have characteristics that gave different results in this study.

Water content

Overall the same proportions of metals were recovered by HNO_3 from 1/3 bar and saturated samples (Table 54). Recovery from saturated samples was significantly lower for Cu and Cd but not in large enough amounts to conclude that water content made any difference in the recovery of added metals by HNO_3.

For DTPA, the effect of water content was much greater, in that the recovery from 1/3 bar samples was significantly greater than from saturated samples for Cu, Ni, Cd, Zn and significantly less for Pb (Table 54). If DTPA extractability is correlated with plant availability these results would say that significantly greater amounts of the trace metals are available in unsaturated soil systems. This is likely due to the formation of relatively insoluble forms of the metals under reducing conditions which can be caused by saturation with water.

In all cases lower concentrations of metals were found in saturation extracts of sludge-amended soils incubated at saturation than in those from 1/3 bar samples (Table 55-58). Again this is likely due to a conversion of the metals from water soluble forms to insoluble forms, i.e. sulfides, in the saturated samples.

Sample Preparation

Sample preparation had significant effects on extractability with all extracts. Recovery by HNO_3 was reduced when the samples were air-dried (Table 54). This was likely due to the formation of less soluble forms of the metals as the samples dried.

Drying the samples significantly increased the extractability of all metals by DTPA (Table 54). A possible explanation here is that on drying some of the organic matter decomposed, releasing metals that could then be extracted by the DTPA. This type of decomposition would not effect the HNO_3 extraction because the HNO_3 treatment was strong enough to remove the metals from the organic fraction of samples incubated at either water content.

In cases where sample preparation had an effect on saturation extract concentrations of metals it was always to increase the metal concentrations (Tables 55-58). The increase was significant for 20 of 28 cases (4 metals x 7 sludges). The explanation given for increased recovery with DTPA could also apply here. Drying would increase oxidation of the organic matter, releasing metals to be extracted by the very mild extracting agent, water.

3.3. ORGANIC MATTER DECOMPOSITION IN SLUDGE-AMENDED SOILS

Rate of decomposition

Experimental

Three soils were mixed with sewage sludge at the rate of 100 mT/ha and incubated at 25 ± 1°C. The soils used (Table 63) were all low in native organic matter, coarse-textured, and represented an acid soil (Baywood), a neutral soil (Delhi), and a calcareous soil (Calhi). Sludges collected from three different sewage treatment plants in Southern California were utilized (Table 64). A quantity (20.1 g) of dried sewage sludge was added to 450 g soil in plastic containers and mixed thoroughly. Water was added to bring the soil water content to that equivalent to 1/3 bar moisture tension (≃5% by weight) or saturation (20-25%). After the water was added, the amended soils were carefully mixed. Six replicates of each treatment were kept in a larger, sealed container and placed in a constant temperature room. A current of CO_2-free, H_2O saturated air was pulled through the system by suction to carry evolved CO_2 to the collector. The collected CO_2 was frequently determined by precipitation of carbonate as $BaCO_3$ and back titration of the excess alkali with standard acid. The CO_2 monitoring was continued for 253 days.

TABLE 63. SOME PROPERTIES OF SOILS USED IN THE EXPERIMENT.

Soil	Classification	pH	CEC	Saturation percentage	C	N	C/N ratio
			meq/100g	----------	%	----------	
Baywood sand	Entic Haploxeroll	5.2	6.5	25.8	0.37	0.026	14.2
Calhi loamy sand	Typic Xeropsamment	8.2	4.0	19.5	0.12	0.016	7.5
Delhi sand	Typic Xeropsamment	7.3	5.0	25.5	0.55	0.061	9.0

TABLE 64. SOME PROPERTIES OF SLUDGES USED IN THE EXPERIMENT.

Sludge	C	N	C/N ratio	Cd	Cu	Ni	Pb	Zn
	----%-----			----------μg/g----------				
Escondido	30.3	3.43	8.9	198	1808	167	667	2917
Ontario	31.4	2.35	13.4	89	588	1878	378	2415
Rialto	33.8	4.13	8.2	11	490	39	289	1493

Results

The loss of organic C from soils with and without sewage sludge treatment as a function of time under different moisture levels is depicted in Fig. 24 and Table 65. At 1/3 bar moisture tension, the sludge-amended soils showed a short initial period of rapid decomposition, usually about a week, then the data conformed very well to equations of the form log C = log a + m log t where a and m are constants which directly proportion to the initial loss of CO_2 and turnover time, respectively. Correlation coefficients for the regression lines ranged from 0.972 to 0.997 (coefficients of determination, r^2, ranged from 0.944 to 0.994) and were significant at 0.001 level. In linear coordinates, this equation takes the form $C = at^m$. In case of controls and sludge-amended soils at saturated moisture, the exponential curves fit to the entire incubation period.

Carbon losses, expressed as percentages of that originally present in the soil-sludge mixtures, are given in Table 66 and 67. After 34 weeks of incubation, generally < 25% organic carbon was lost. The exception was for the Rialto amended Baywood soil incubated at 1/3 bar where 34.9% of the organic carbon was lost.

Differentiating the function for accumulative carbon loss of the form $C = at^m$ yields the rate function

$$\frac{dC}{dt} = amt^{(m-1)} \qquad (27)$$

Equations of this form were used to calculate the data of Tables 68 and 69. Rates of loss were increased by sludge application. Rates of loss were initially high when the soils were incubated at 1/3 bar tension, however, these rates declined rapidly as the incubation time increased. Rates of

TABLE 65. EQUATIONS DESCRIBING CUMULATIVE CO_2 LOSS FROM SLUDGE-AMENDED SOILS AS INFLUENCED BY INCUBATION TIME.

Soil	Sludge	Time interval (day)	Equation	$r^{2\dagger}$
		Incubated at 1/3 bar moisture tension		
Delhi	0	0 - 249	$C = 11.48t^{0.571}$	0.982
	Rialto	6 - 249	$C = 136.1t^{0.483}$	0.986
	Ontario	8 - 249	$C = 47.53t^{0.633}$	0.987
	Escondido	8 - 249	$C = 93.54t^{0.486}$	0.994
Calhi	0	0 - 253	$C = 2.80t^{0.554}$	0.975
	Rialto	9 - 253	$C = 191.6t^{0.353}$	0.973
	Ontario	9 - 253	$C = 93.86t^{0.415}$	0.984
	Escondido	9 - 249	$C = 139.4t^{0.330}$	0.957
Baywood	0	0 - 253	$C = 30.74t^{0.294}$	0.961
	Rialto	6 - 253	$C = 122.6t^{0.544}$	0.994
	Ontario	6 - 253	$C = 56.26t^{0.536}$	0.944
	Escondido	5 - 253	$C = 86.49t^{0.492}$	0.979

(Continued)

Table 65 (Continued)

Soil	Sludge	Time interval (day)	Equation	r^2
		Incubated under saturated condition		
Delhi	0	0 - 249	$C = 0.94t^{0.982}$	0.981
	Rialto	0 - 249	$C = 6.94t^{1.026}$	0.994
	Ontario	0 - 249	$C = 3.79t^{0.956}$	0.996
	Escondido	0 - 249	$C = 5.36t^{0.981}$	0.992
Calhi	0	0 - 253	$C = 0.58t^{0.760}$	0.940
	Rialto	0 - 253	$C = 7.27t^{0.928}$	0.994
	Ontario	0 - 253	$C = 1.60t^{1.059}$	0.992
	Escondido	0 - 249	$C = 4.81t^{0.904}$	0.983
Baywood	0	0 - 253	$C = 5.78t^{0.574}$	0.974
	Rialto	0 - 253	$C = 10.09t^{0.889}$	0.991
	Ontario	0 - 253	$C = 3.91t^{0.942}$	0.989
	Escondido	0 - 253	$C = 9.23t^{0.817}$	0.974

† All r^2 values are significant at 0.001 level.

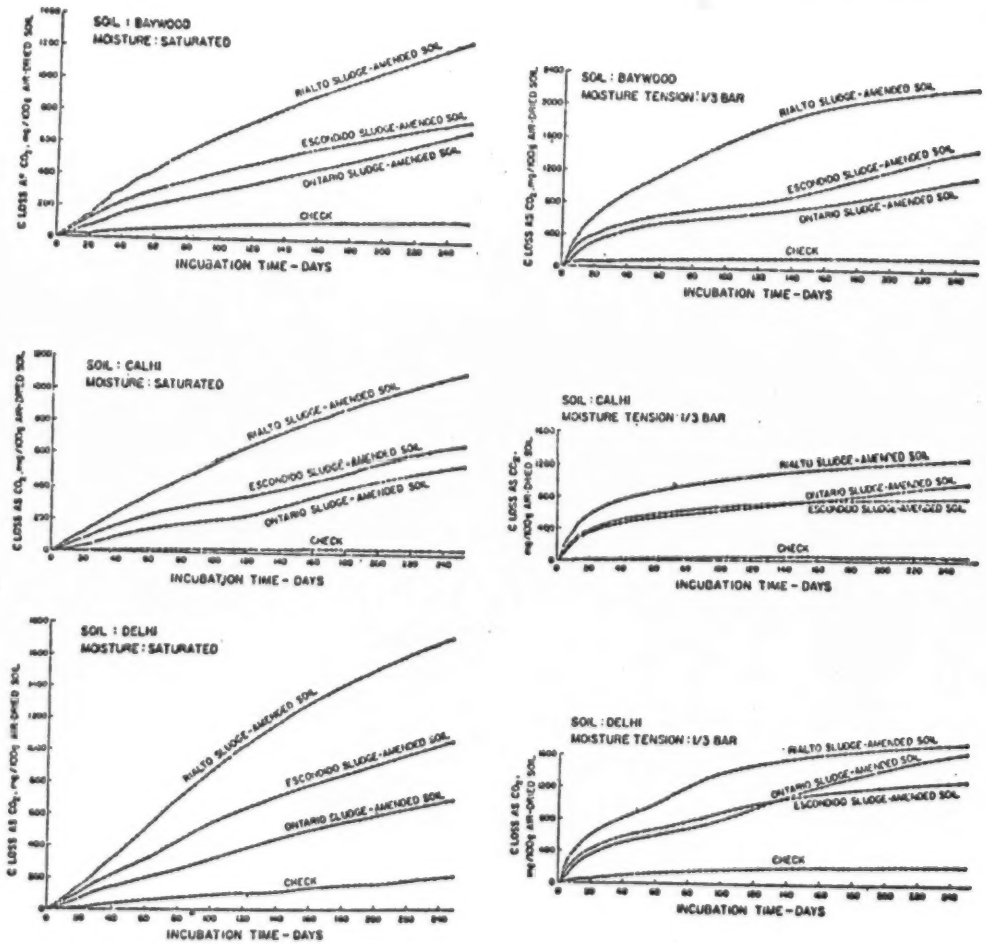

Figure 24. Cumulative C loss from sewage sludge amended soils as a function of time.

TABLE 66. PERCENTAGE LOSS OF ORGANIC CARBON IN SLUDGE-AMENDED SOILS INCUBATED AT 1/3 BAR MOISTURE TENSION

Soil	Sludge	Percentage loss of C at incubation time (week) specified					
		2	4	10	18	26	34
Delhi	0	2.6	3.8	6.4	9.0	11.1	13.0
	Rialto	6.4	9.0	14.0	18.6	22.3	25.3
	Ontario	3.5	5.5	9.8	14.2	17.9	21.2
	Escondido	4.8	6.8	10.6	14.1	16.8	19.2
Calhi	0	2.7	4.0	6.7	9.3	11.4	13.2
	Rialto	8.1	10.4	14.4	17.7	20.1	22.1
	Ontario	5.0	6.7	9.8	12.5	14.6	16.3
	Escondido	6.2	7.8	10.5	12.7	14.4	15.7
Baywood	0	4.9	6.0	7.9	9.4	10.5	11.3
	Rialto	7.5	10.9	17.9	24.7	30.2	34.9
	Ontario	3.6	5.2	8.4	11.6	14.1	16.3
	Escondido	5.0	7.1	11.1	14.8	17.7	20.2

TABLE 67. PERCENTAGE LOSS OF ORGANIC CARBON IN SLUDGE-AMENDED SOILS INCUBATED UNDER SATURATED CONDITION

Soil	Sludge	Percentage loss of C at incubation time (week) specified					
		2	4	10	18	26	34
Delhi	0	0.6	1.2	3.0	5.4	7.7	10.1
	Rialto	1.4	2.8	7.2	13.1	19.1	25.2
	Ontario	0.7	1.3	3.1	5.4	7.7	9.9
	Escondido	1.0	2.0	5.0	8.8	12.7	16.5
Calhi	0	1.0	1.7	3.3	5.2	6.9	8.4
	Rialto	1.4	2.7	6.3	10.8	15.2	19.5
	Ontario	0.5	1.0	2.6	4.8	7.1	9.4
	Escondido	1.0	1.8	4.1	7.1	9.8	12.5
Baywood	0	1.9	2.9	4.9	6.8	8.4	9.9
	Rialto	1.5	2.8	6.4	10.8	15.0	19.0
	Ontario	0.7	1.4	3.3	5.7	8.1	10.4
	Escondido	1.3	2.2	4.7	7.6	10.3	12.8

TABLE 68. RATE OF C LOSS FORM SLUDGE-AMENDED SOILS INCUBATED AT 1/3 BAR MOISTURE TENSION

Soil	Sludge	Rate of C loss at incubation time (week) specified					
		2	4	10	18	26	34
		mg C/100 g soil/day					
Delhi	0	0.58	0.43	0.29	0.22	0.19	0.17
	Rialto	4.58	3.20	1.99	1.47	1.22	1.06
	Ontario	3.12	2.42	1.73	1.39	1.22	1.10
	Escondido	3.19	2.24	1.40	1.03	0.85	0.74
Calhi	0	0.13	0.10	0.06	0.05	0.04	0.04
	Rialto	3.34	2.14	1.18	0.81	0.64	0.53
	Ontario	2.27	1.51	0.88	0.63	0.51	0.43
	Escondido	2.14	1.35	0.73	0.49	0.38	0.32
Baywood	0	0.38	0.23	0.12	0.08	0.06	0.05
	Rialto	5.46	3.98	2.62	2.00	1.70	1.50
	Ontario	2.42	1.75	1.15	0.87	0.74	0.65
	Escondido	3.04	2.14	1.34	0.99	0.83	0.72

TABLE 69. RATE OF ORGANIC CARBON LOSS FROM SLUDGE-AMENDED SOILS INCUBATED UNDER SATURATION CONDITION

Soil	Sludge	Rate of C loss at incubation time (week) specified					
		2	4	10	18	26	34
		mg C/100 g soil/day					
Delhi	0	0.24	0.24	0.23	0.23	0.23	0.23
	Rialto	2.08	2.12	2.17	2.20	2.22	2.24
	Ontario	0.88	0.85	0.82	0.80	0.79	0.78
	Escondido	1.36	1.35	1.32	1.31	1.30	1.29
Calhi	0	0.06	0.05	0.04	0.04	0.03	0.03
	Rialto	1.52	1.45	1.36	1.30	1.26	1.24
	Ontario	0.54	0.56	0.59	0.61	0.63	0.64
	Escondido	0.92	0.86	0.79	0.75	0.72	0.70
Baywood	0	0.29	0.22	0.15	0.12	0.10	0.09
	Rialto	1.83	1.69	1.53	1.43	1.37	1.33
	Ontario	0.86	0.83	0.79	0.76	0.74	0.73
	Escondido	1.27	1.12	0.95	0.85	0.79	0.76

loss were more stable when the soils were incubated under saturation conditions.

Discussion

The initial losses of organic carbon from saturated samples were consistently lower than those from 1/3 bar moisture tension soils (Table 68 and 69). A sharp release of heavy metals from unsaturated samples due to the breakdown of water-insoluble organo-metalic complexes could supply metals with a result of groundwater contamination and/or hazardous effects to plant growth. A gradual release of heavy metals from saturated soils and the associated lower metal concentration may be safer in this regard.

The magnitude of sludge influence depends upon chemical properties of sludges, soil moisture, and soil reactions. Rialto sludge contained the lowest concentrations of metal and appeared to provide for the greatest increase in carbon release. In most cases, Escondido sludge which contained relatively high quantities of Cd and Cu seems to be the less favorable source of substrate for soil microbiological activities. The carbon losses from Ontario sludge-amended soils were initially less than those from Escondido sludge-amended soils. For neutral and calcareous soils incubated at 1/3 bar moisture tension, C losses from Escondido sludge-amended soils were surpassed by those from Ontario sludge-amended soils after 4.5 and 5 months, respectively (Fig. 24). Enhancing effect of Escondido and Ontario sludges on neutral soil was slightly higher than that on acid soil. The latter, however, showed the most pronounced effect of Rialto sludge.

Native organic carbon of the acid soil was very stable (Table 66); although fungi, the dominant microbial group in acid soil, are known to be capable of breaking down cellulose and lignin which are resistant to bacterial degradation. For the calcareous soil, in which the dominant microbial group is likely bacteria, the rate of C loss was smaller initially but by the 18th week of incubation there was no difference and at the 34th week was greater than that of the acid soil at 1/3 bar moisture tension. Furthermore, even though initial losses and rates of C loss from sludge-amended Calhi soils (incubated at 1/3 bar moisture tension) were higher in relation to the control, the turn-over time ranged from 2 to 7 times as long. A full interpretation for this negative influence cannot be made from the results of this study.

Conclusion

Soils incubated at 1/3 bar moisture tension yielded a large organic carbon breakdown for a short period of time while under saturated condition, the decomposition was slower but more consistent. Sludge amendment

resulted in greatly increased carbon release when soil moisture was at 1/3 bar moisture tension.

Spectra Analysis of Soluble Products of Decomposition

There are two principle types of transformation to be expected in the soil environment after an anaerobically digested sewage sludge has been applied to agricultural land. The first reaction is abiotic in nature and is characterized by reactions which occur in the aqueous phase of a soil to bring about chemical equilibrium with an anthropogenic material. The second kind of transformation is mediated biologically and is characterized by transformations involving especially organic components of the sludge. These processes usually will not be rapid and will be controlled by many factors including soil microbial population, the nature of the sludge, soil pH, soil water content and temperature.

A number of recent studies have been focused on the effects of relatively long-term microbial degradation of sewage sludge in the soil environment because these effects are related directly to the evaluation of sludge as a source both of plant nutrients and trace metal contaminants. The microbial degradation of sewage sludge generally can result in the production or release of plant-available N, P, and S (see, e.g., Epstein et al., 1977; Elseewi et al., 1977; Tester et al., 1977, 1979). On the other hand, Hohla et al. (1978) have observed in lysimeter studies that heavy applications of anaerobically digested sewage sludge can produce high levels of oil and grease C in the upper part of the soil profile, as well as produce significant increases in the concentration of carbohydrate C in leachate waters. These changes could have an adverse impact on soil productivity. The same can be said for the transformations of the trace metal components in sludges, such as Cd, Cu, Pb, and Zn, although the behavior of these metals during the course of sludge degradation is complicated (Bloomfield and Pruden, 1975; Lagerwerff et al., 1977; Silviera and Sommers, 1977). A principal conclusion that can be drawn from the published data on the changes in the forms of plant nutrient and toxic elements during the decomposition of sewage sludge in soil is that a complex set of biologically-mediated reactions involving the organic components of sludge must be understood better in order to predict the fates of the inorganic components.

In particular, the transformations involving potentially hazardous trace metals would seem to be connected intimately with changes in metal-complexing functional groups in the sludge organic fractions as these fractions are altered by microbial activity (Page, 1974; Silviera and Sommers, 1977). No experimental data exist which can provide direct information about these changes in organic components in soils. This study represents an initial step in providing some of these data through a qualitative infrared spectroscopic study of the water soluble

compounds extracted periodically from soil-sludge mixtures which were incubated at 25°C for 100 weeks.

Experimental Procedures

Two soils and two sewage sludges were employed in the study. The characteristics of the soils are given in Table 70. The principle difference between the two soils is soil pH. Baywood represents a relatively acidic soil whereas Calhi is alkaline. The two sludges employed in the experiment were collected from the sludge drying beds at the Ontario and Rialto wastewater treatment plants in southern California. Representative data on the trace metal and phosphorus content of these anaerobically digested sludges has been published (Holtzclaw et al., 1976, 1978). Ontario sludge was relatively higher in trace metal content while Rialto contained higher levels of phosphorus. The total N and S percentages in the sludges were 2.8% N and 1.2% S (Ontario) and 2.2% N and 1.0% S (Rialto).

The soil and sludge samples were air-dried and crushed so as to pass a 2-mm sieve. The two sludges then were mixed with the two soils at a rate equivalent to 100 T/ha to yield four different soil-sludge combinations. The mixtures were placed in 500 ml plastic containers and water was added to bring the water content either to the equivalent of field capacity (1/3-bar soil water tension) or to complete saturation (free water on the soil surface). The moist, sludge-amended soil samples were placed in a constant temperature room and incubated at 25°C. Water was added as necessary during the incubation period to maintain the water content at the predetermined level. Each different combination of soil, sludge, and water content was incubated in triplicate.

Periodically, sample containers were removed from the constant temperature room and saturation extracts were prepared from the sludge-amended soils. The saturated samples were placed directly in a Richards funnel and the extract was collected. In the case of the 1/3-bar samples, distilled water was added to bring them to saturation. These samples were allowed to equilibrate for two hours before being extracted. Saturation extracts were prepared in this manner after incubation periods of 1 day, 2, 4, 10, 18, 26, 34, 50 and 100 weeks.

Aliquots of the saturation extracts were prepared for infrared spectral analysis by filtering them through Watman No. 42 ashless filter paper, then adding NaN_3 at a concentration of 0.02% in order to inhibit bacterial growth and prevent further metabolism of organic constituents by microorganisms. Infrared spectra then were recorded for combined aliquots composed of equal volumes of filtered extracts taken from the triplicated incubation samples.

Spectra were obtained for solid films produced by placing about 0.6 ml of the combined aliquots on a AgCl plate and then evaporating

TABLE 70. SOME CHARACTERISTICS OF THE SOILS EMPLOYED IN THE INCUBATION STUDY.

Soil	Sand	Silt	Clay	pH*	Organic carbon content	1/3 bar moisture content	Saturation percentage	Cation exchange capacity
	-------- % --------				---------- % ----------			meq/100 g
Baywood	98.0	1.0	1.0	5.2	1.29	7.3	25.8	6.5
Calhi	82.0	15.0	3.0	8.2	1.06	5.7	19.5	4.0

* 1:1 soil-water mixture

the solution to dryness over P_2O_5 in a vacuum desiccator kept in total darkness. The spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer in the 4000 to 400 cm^{-1} wavenumber range. A blank AgCl plate was utilized in the reference beam. Reference spectra of a 50 m polystyrene film recorded at the same time were used to correct the spectra for systematic error in the spectrophotometer. Interpretation of the spectra was carried out with the assistance of standard references (Pasto and Johnson, 1969; Nyquuist and Kagel, 1971; Stevenson and Goh, 1971; Williams and Fleming, 1973; Silverstein et al., 1974; Bellamy, 1975). In assessing the changes in the organic compounds in the saturation extracts during incubation, the 1-day extract was designated as the "zero-time" sample. This extract was selected on the basis of the assumption that many of the chemical and physical equilibria affecting the organic compounds should be achieved in one day, while microbial degradation should not yet be significant.

Results

The infrared (IR) spectra in the 2200 to 500 cm^{-1} wavenumber range for the saturation extracts obtained from several of the eight different soil-sludge-water content combinations are shown in Fig. 25 - 31. The IR spectra in the 4000 to 2200 cm^{-1} range were virtually identical for all of the saturation extracts and, therefore, are not shown. The general features of the zero-time IR spectra (1 day) are similar to those in the IR spectra of purified fulvic acid fractions of Ontario and rialto sludges (Sposito et al., 1976; Baham et al., 1978; Sposito et al., 1978). The previous interpretation of the spectra of sludge-derived acid, therefore, may be applied to help analyze the data in Fig. 25 - 31. However, since the saturation extracts of the incubated soil-sludge mixtures contained dissolved inorganic salts as well as organic compounds, the interpretation of the IR spectra in Fig. 25 - 31. necessarily will be more complicated and less certain than that of the IR spectrum of fulvic acid alone. The discussion which follows thus reflects a qualitative analysis which, although detailed, cannot be regarded as completely definitive without additional, confirming experimental data. A summary of the principal band assignments used as guides in the interpretation of the spectra is presented in Table 71.

Effect of Time--The effect of incubation time on the IR spectrum of the water-soluble fraction of Rialto sludge mixed with Calhi soil at 1/3-bar soil water tension is shown in Fig. 25. The IR spectra for Ontario sludge with the same combination of soil and water content (not shown) exhibited the same trends. The major features in the spectrum of the zero-time extract in Fig. 25 are: (1) a shoulder absorption at 1725 cm^{-1}, which may be assigned to C = O in carboxyl groups, and a strong, broad absorption centered at 1633 cm^{-1} that probably represents both amide and carboxylate groups; (2) a shoulder absorption at 1560 cm^{-1} that may be attributed to amide groups; (3) a weak absorption at 1413 cm^{-1} that is consistent with the presence of

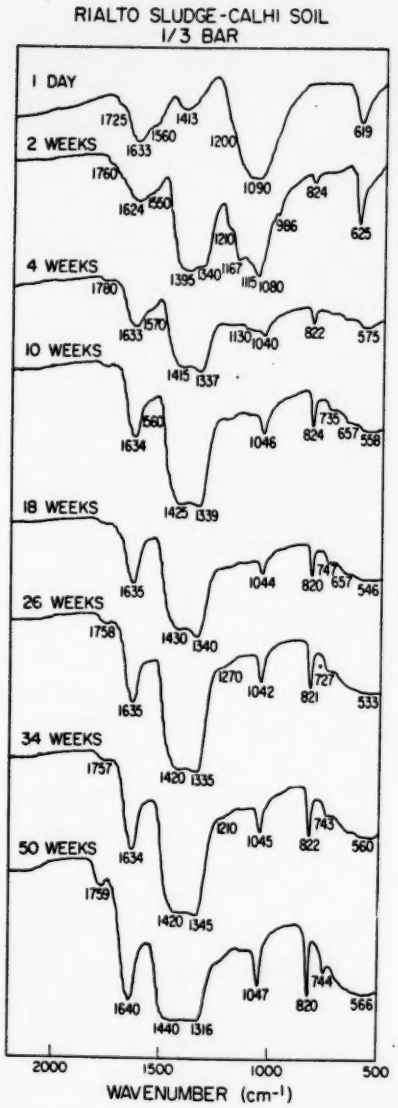

Fig. 25. The IR spectra of saturation extracts taken from a Rialto sludge-Calhi soil mixture incubated at a water content equivalent to 1/3 bar soil water tension.

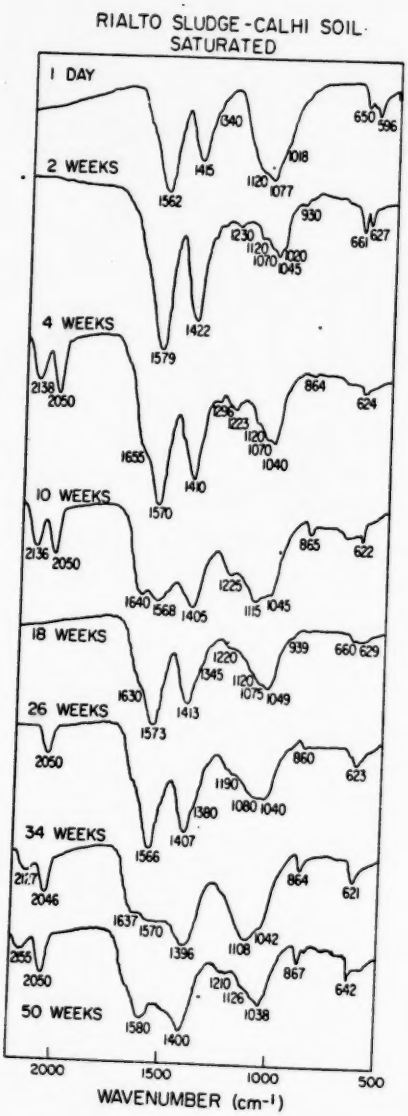

Fig. 26. Infrared spectra of saturation extracts as in Fig. 25 except that the soil-sludge mixture is water-saturated.

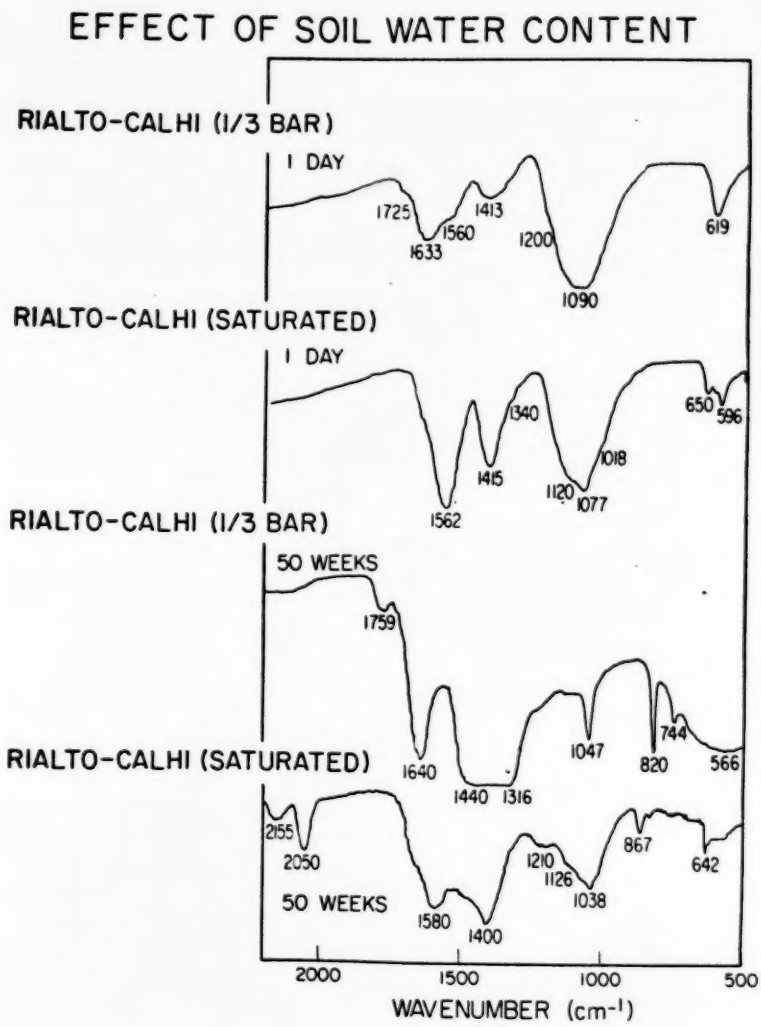

Fig. 27. Comparison of the IR spectra of the saturation extracts taken from Rialto sludge-Calhi soil incubated at 1/3 bar and saturated water conditions.

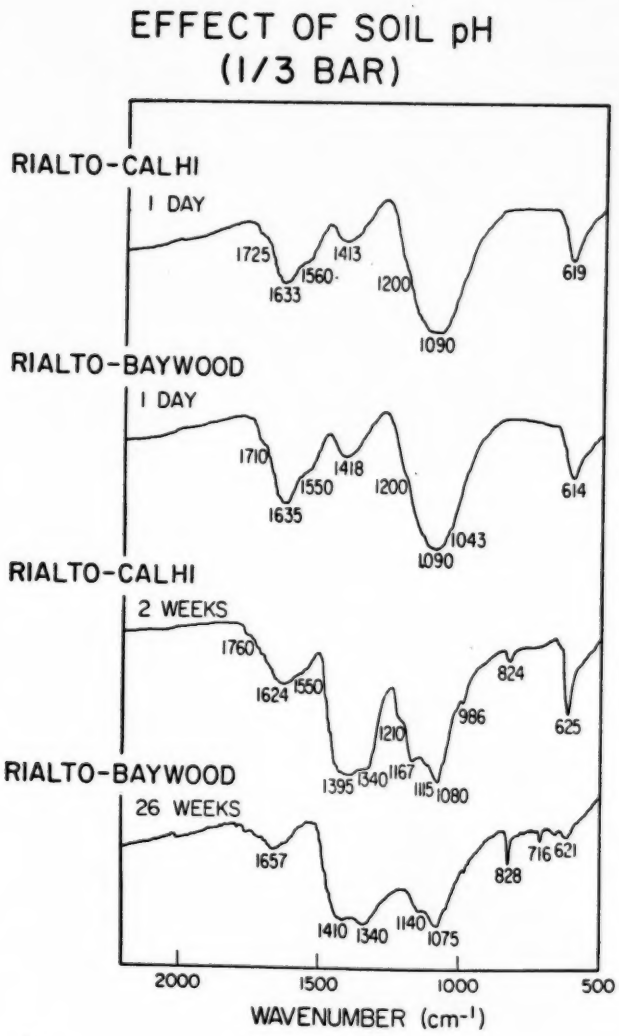

Fig. 28. Comparison of the IR spectra of the saturation extracts taken from Rialto sludge incubated at 1/3 bar soil water tension in Baywood and Calhi soil.

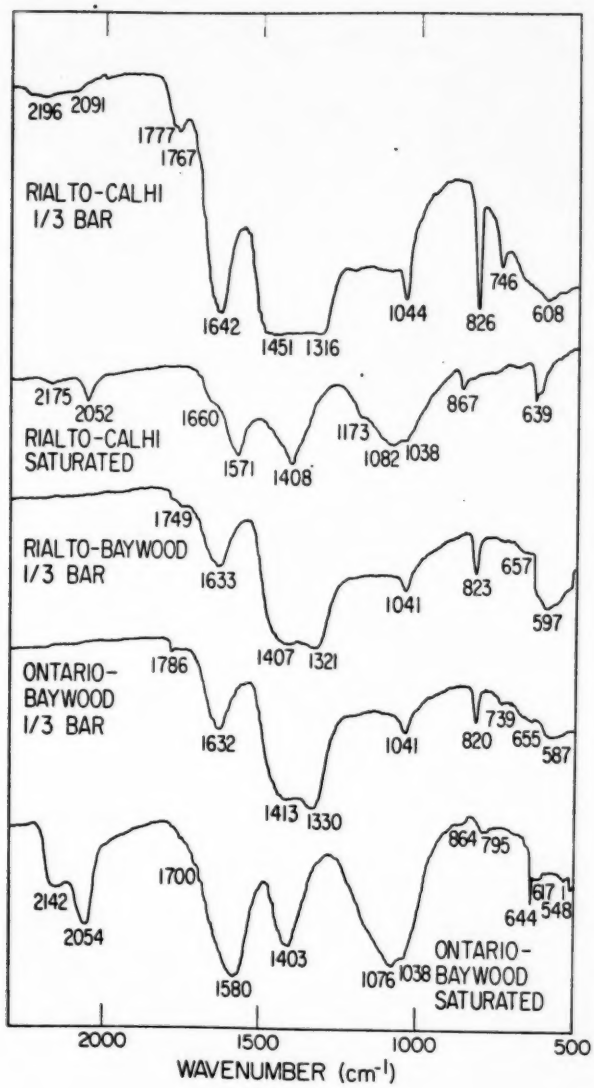

Fig. 29. The IR spectra of saturation extracts taken from several different sludge-soil mixtures incubated at 25° C for 100 weeks.

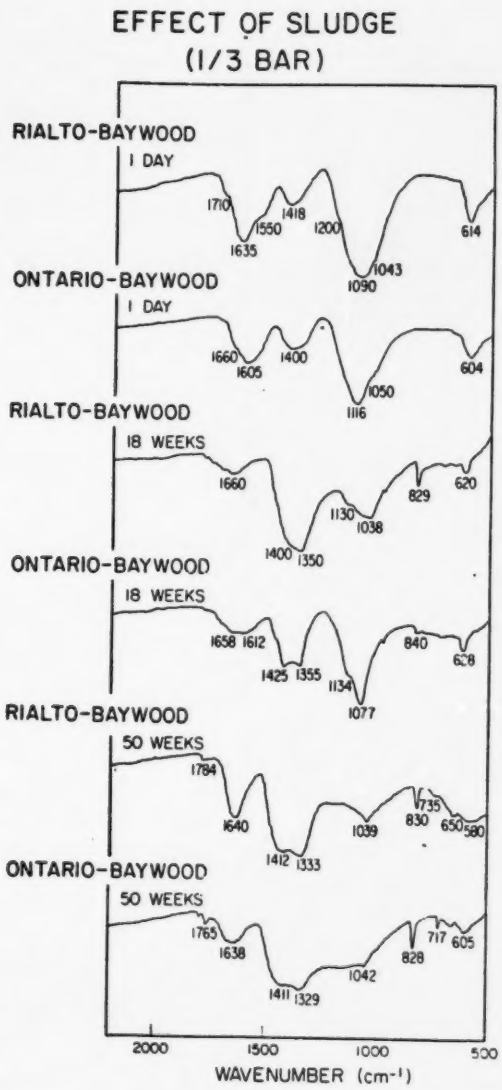

Fig. 30. Comparison of the IR spectra of saturation extracts taken from Rialto sludge and Ontario sludge incubated under identical soil and water conditions.

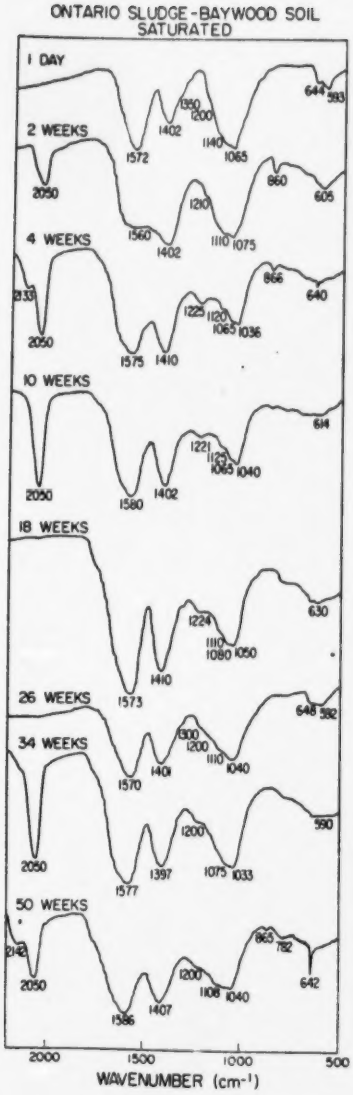

Fig. 31. The IR spectra of saturation extracts taken from an Ontario sludge-Baywood soil mixture incubated under saturated water conditions.

carbonate, carboxylate, phenolic compounds, and/or ammonium ion; (4) a strong, very broad band beginning at 1250 cm^{-1}, centered at 1090 cm^{-1}, and ending at 850 cm^{-1}, which could represent contributions from polysaccharides, sulfonates, sulfates, phosphates, and silicates, and (5) a sharp, medium band at 619 cm^{-1} that may ba assigned to sulfonate and/or sulfate absorptions. The band assignments to carboxylate, amide, and sulfonate groups are consistent with the previously demonstrated presence of these functional groups in Rialto fulvic acid (Sposito et al., 1976; Holtzclaw and Sposito, 1978, 1979; Sposito et al., 1978a). Similarly, the contribution of polysaccharides to the band at 1090 cm^{-1} is corroborated by both IR and NMR spectra of the fulvic acid fraction (Sposito et al., 1976, 1978a) and by chemical analysis of a saturation extract of Rialto sludge (J. E. Baham, unpublished data). The presence of carbonate in the saturation extract is likely because the Calhi soil is calcareous. However, the characteristic absorptions of carbonate at 1410-1490 cm^{-1} and 860-880 cm^{-1} cannot be distinguished separately in the spectrum and certain identification is not possible.

After two weeks of incubation, definite changes are observed in the IR spectrum of the saturation extract. The principal developments include: (1) a weakening of the amide I and amide II bands (Cf. Table 71); (2) the appearance of a strong, broad band between 1340 and 1395 cm^{-1}; (3) a weakening and improved resolution of the broad band at 1090 cm^{-1} into components at 1210, 1167, 1115, and 1080 cm^{-1}, and (4) the emergence of a weak, sharp band at 824 cm^{-1}. The new broad band noted in (2) may represent NO_3^- and/or CO_3^{2-} produced as the sludge decomposes, since both of these anions absorb strongly around 1350-1400 cm^{-1}. However, the confirming absorptions for the anions in the 800-900 cm^{-1} region are not unequivocably present in the spectrum: the required CO_3^{2-} band near 850 cm^{-1} is at best a shoulder feature and the required, sharp NO_3^- band near 820 cm^{-1} may be confused with an equally sharp band at the same position that is produced by phosphate esters (see below). The assignment to NO_3^- is probably the better choice here, inasmuch as both of the required bands for this anion can be discerned and the presence of NO_3^- is consistent with the decrease in amide absorptions, noted in (1) above. The existence of bands at 1210, 1167, and 625 cm^{-1}, as well as the shoulder features on the 1080 cm^{-1} band, are consistent with the continued presence of sulfonate compounds in the saturation extract. However, since SO_4^{2-} also absorbs around 1100 cm^{-1} and 620 cm^{-1}, it may be present as well.

The IR spectrum after four weeks of incubation is significantly different, in the fingerprint region, from the zero-time spectrum. In particular, the broad band between 1337 and 1415 cm^{-1} dominates the spectrum, with only weak, sharp absorptions around 1040 and 820 cm^{-1} remaining in the region below 1090 cm^{-1}. Thus the four-week spectrum may be interpreted to represent contributions from carboxylate groups (1633 and 1400 cm^{-1}), NO_3^-, and, possibly organic phosphate (1040 and 822 cm^{-1}). Both NH_4NO_3 and aliphatic phosphate esters can produce sharp bands near 1040 and 820 cm^{-1}, and both types of compound are

TABLE 71. PRINCIPAL BAND ASSIGNMENTS IN THE IR SPECTRA OF SATURATION EXTRACTS OBTAINED FROM INCUBATED SOIL-SLUDGE MIXTURES.

Band position cm^{-1}	Assignment
2130, 2050	azide
1760-1710	C=O in carboxyl
1700-1630	C=O (Amide I)
1655-1620	NH_2 deformation (Amide II, 1°)
1650-1550	COO^- (carboxylate)
1570-1515	NH_2 deformation (Amide II, 2°)
1490-1410	CO_3^{2-}
1430-1390	NH_4^+
1400-1310	COO^-; phenolic compounds
1380-1350	NO_3^-
1350-1342	SO_3H (sulfonic acid group)
1300	HCO_3^-
1260-1150	SO_3^- (sulfonate)
1200	phenolic compounds
1165-1150	SO_3H
1130-1080	SO_4^{2-}
1100-1000	PO_4^{3-} (inorganic phosphate)
1080-1010	SO_3^-
1090-1040	C-O in polysaccharide; Si-O
1050-970	P-O-C (aliphatic organic phosphate)
880-830	CO_3^{2-}
840-815	NO_3^-
830-740	P-O-C
750-720	NO_3^-
680-610	SO_4^{2-}
600-700	SO_2 deformation in SO_3^- or SO_3H

expected as synthesis products of sludge degradation. All of these features persist and become much better defined in the 10-week spectrum. Granting the accuracy of the band assignments, it may be concluded that, after ten weeks of incubation, the principal constituents identifiable by IR spectra are carboxylates and nitrates, although carbonates and organic phosphates should not be ruled out completely. Of equal importance is the conclusion that proteinaceous and carbohydrate constituents have disappeared, as have the sulfonate compounds known to be present initially in Rialto sludge. These more labile components of the sludge thus were degraded relatively quickly under the imposed soil conditions of high alkalinity and moderate water content. The sulfonate decomposition rate observed in these experiments is not as rapid as was indicated in the degradation studies of Swisher et al. (1979), who found that linear alkyl benzene sulfonates (LAS) and their breakdown products disappeared after only ten days' incubation in river water. The longer time required in the Calhi soil is consistent with the results of Inoue et al. (1978), who showed that adsorption of LAS by soil minerals can inhibit its degradation.

The subsequent IR spectra are quite similar to the 10-week spectrum. The band around 720-740 cm^{-1}, which is discernible in the 10-week spectrum, persists throughout the following forty weeks. This band is characteristic of NO_3 compounds and, therefore, it supports the assignment of the bands near 1040 and 820 cm^{-1}, which grow in prominence with it, to NO_3^-. The IR spectrum after 50 weeks of incubation indicates the presence of carboxyl groups (weak absorption at 1759 cm^{-1}), carboxylates, and nitrates. Absorptions from protein, carbohydrate, and sulfonate and/or sulfate compounds have disappeared completely. The 100-week spectrum (top of Fig. 29) is almost identical with the 50-week spectrum. Thus the majority of changes in the water-soluble fraction seem to be completed within about ten weeks of incubation.

Effect of Water Content--The effect of increased water content on the degradation of the sludges is illustrated by the IR spectra in Figs. 26 and 27, which refer again to Rialto sludge mixed with Calhi soil. The spectra for Ontario sludge mixed with the same soil at the same water content (not shown) were similar. Examination of Fig. 27 shows that the zero-time (1 day) IR spectrum of the saturation extract taken from the water-saturated, Rialto sludge-Calhi soil sample is somewhat different from that of the saturation extract taken from the Rialto sludge-Calhi soil sample maintained at 1/3-bar soil water tension. The main features in the zero-time spectrum in Fig. 26 include: (1) broad, deep bands centered at 1562 and 1415 cm^{-1}, which likely represent contributions from amide groups and carboxylates; (2) a strong band beginning at 1250 cm^{-1}, centered at 1077 cm^{-1} with a shoulder at 1120 cm^{-1}, and ending at about 850 cm^{-1}, and (3) a weak doublet at 650 and 596 cm^{-1}. The very broad absorption at 1077 cm^{-1} probably reflects the presence of polysaccharides and sulfonates, as well as carbonates and sulfates,

although completely definitive assignments cannot be made. The principal reason for the deeper absorptions in the wavenumber region between 1700 and 1300 cm^{-1} in the zero-time spectrum of the saturated sample is believed to be the selective extraction of proteinaceous compounds and organic acids from sludge with water (J. E. Baham, unpublished data), which should increase with the degree of saturation of the soil.

The IR spectra in Fig. 26 of the extracts taken between two weeks and 34 weeks after incubation began show relatively little qualitative change, with one notable exception: a double absorption at 2138 and 2050 cm^{-1} is observed frequently. It is quite possible that this feature is an artifact produced by the NaN_3 which was added to the saturation extracts to prevent microbial action. The double absorption is in a wavenumber region where almost no other functional groups absorb and it closely matches the known spectral pattern for NaN_3 (Sadtler Standard Spectra, 1962). Moreover, in a separate experiment in which certain of the saturation extracts were divided, with one-half treated by NaN_3 and one half by $AgNO_3$, the two absorptions appeared only in the spectrum of the extract to which NaN_3 had been added. Nonetheless, the appearance of these bands is somewhat puzzling because the concentration of the azide added to prevent microbial growth is so small and because the bands appear in some spectra but not in others. One possible explanation is related to the fact that the intensity of the azide band depends on the nature of the compound to which azide is bonded or complexed (Patai, 1971). There may be metabolic breakdown products from the sludge reacting in some fashion with the added azide to yield complexes with strongly-absorbing azide groups. As the concentrations of these products change during incubation, so may the intensity of the azide absorption.

The IR spectra after 50 weeks in Fig. 27 and that for the extract taken after 100 weeks (Fig. 29) are not very much like the later 1/3 bar spectra. In particular, it appears that the compounds reflected in the zero-time spectrum in Fig. 27 and known to be present initially in the sludge (e.g., proteinaceous material, polysaccharides, and sulfonates) either are not degrading as rapidly as they did in the 1/3-bar mixtures or are being resynthesized about as rapidly as they are degraded. In addition, the bands indicative of NO_3^- are much less pronounced in, e.g., the 50-week spectrum in Fig. 26 as compared with the 50-week spectrum in Fig. 25. Given the relatively less aerobic conditions in the saturated Rialto sludge-Calhi soil mixtures, the general impression is that microbial degradation of the sludge has been retarded.

Effect of soil pH value--The effect of incubation of Rialto sludge in the acidic Baywood soil at 1/3 bar soil water tension is illustrated in Fig. 28. The zero-time IR spectrum is almost identical with that of Rialto sludge-Calhi soil at 1/3 bar, and the same kinds of probable band assignments may be made. Moreover, the same major changes appear to be occurring in the Baywood saturation extract during incubation,

but at a much lower rate than in the Calhi extract. For example, the two-week Rialto sludge-Calhi soil spectrum resembles the 26-week Rialto sludge-Baywood soil spectrum. In particular, the amide, polysaccharide, sulfonate and/or sulfate absorptions are more persistent in the latter spectrum. The amide II band is still evident in the 10 week spectrum (not shown), while the polysaccharide absorption and the sulfonate and/or sulfate absorption at 620 cm^{-1} persist at least for 26 weeks. These absorptions were essentially absent from the ten-week Rialto sludge-Calhi soil spectrum (Fig. 25). Aside from the differences in their rate of appearance, the major transformation products (carboxylate and nitrate) appear to be the same in both cases. The 100-week (Fig. 29) spectra of Rialto sludge-Calhi soil and Rialto sludge-Baywood soil both show the same principal absorptions, which suggests that similar reactants have been consumed and similar products have been formed.

Effect of sludge characteristics--The relative lack of effect of sludge characteristics on the decomposition process may be seen by examining Fig. 30 which compares spectra obtained for Rialto and Ontario sludes under the same soil (Baywood) and water (1/3 bar) conditions. Although there are some small differences in the shapes of the spectral bands after 50 weeks both spectra are quite similar.

Conclusions

The microbial decomposition of anaerobically-digested sewage sludge, as inferred through changes in the IR spectra of saturation extracts taken from soil-sludge mixtures incubated under laboratory conditions, appeared to follow a pattern which involved the disappearance of carbohydrate, protein, sulfonate and/or sulfate compounds, with the emergence of carboxylates and nitrates. Under relatively optimal conditions of soil reaction and water content, these transformations were essentially complete after 10 weeks. When the soil reaction was acidic, the same decomposition processes appeared to be taking place as occurred in the alkaline soil, but their rates were lower, evidently because of the adverse effect of protons on bacterial activity. Under water-saturated soil conditions, the rate of sludge decomposition appeared to be greatly retarded. Thus it may be concluded that the degradation of the water-soluble fraction of sewage sludge will be the least advanced in the case where the soil is both acidic and water-logged. This conclusion is exemplified by the IR spectra shown in Fig. 31, which are of the saturation extracts taken from Ontario sludge-Baywood soil mixtures maintained at complete water saturation. The zero-time spectrum in Fig. 31 is quite comparable with that shown at the top of Fig. 26. However, even after 50 weeks, all the major absorptions present in the one-day spectrum are still evident. (As in all the other water-saturated samples, azide bands appear in some of the later spectra.) After 100 weeks (Fig. 29), the IR spectrum of the extract remains substantially unchanged.

CHAPTER 4

FRACTIONATION OF TRACE METALS IN SLUDGE-AMENDED SOILS

4.1. EVALUATION OF METAL FRACTIONATION PROCEDURES

As has been pointed out by Stover et al. (1976), trace metals in sludges and sludge-amended soils are expected to be retained within distinct fractions. These are:

1) The cation exchange complex of mineral and organic materials;

2) The adsorption surfaces of hydrous oxides or surfaces with a similar structure;

3) The functional groups on organic constituents; and

4) The precipitated metal carbonates and sulfides.

In undisturbed sludge-amended soils and in moist incubated soil-sludge mixtures a small proportion of the total metal content may be present in the soil solution.

Stover et al. (1976) proposed a fractionation procedure to distinguish the solid-bound metals in whole sludges. In this procedure metals held by exchange sites were removed using a KNO_3 solution, adsorbed metals were assumed to be extracted with KF solution, organic-bound metals with a solution of sodium pyrophosphate, carbonates with EDTA and sulfides with HNO_3. The extraction of exchangeable metals using KNO_3 solution was based on established methods for soil analysis. The use of other extractants was evaluated using pure metal carbonates and sulfides, and suggested a greater or lesser degree of differentiation for the organic-, carbonate-, and sulfide-bound forms. It seems unlikely, however, that KF will extract adsorbed metals as fluoride complexes with the metals under consideration (Ca, Cu, Ni, Pb and Zn) are appreciably less stable than comparable OH complexes (Sillen and Martell, 1966) expected to be involved in metal adsorption on hydrous oxide surfaces. Furthermore, a more complete extraction of organic-bound metals is expected to be achieved with NaOH solution. It is possible that these limitations contributed to the generally incomplete recovery of total metals using the procedure proposed by Stover et al. (1976).

Proposed modifications to the Stover procedure involve the use of distilled water washing in the removal of adsorbed metals and the

adoption of a 0.5 M NaOH extraction for organic-bound metals. The potential of distilled-water washing in the removal of adsorbed metals was suggested by the dependence of the extent of metal adsorption by hydrous oxide surface on the ionic strength of the contacting solution (Bowden et al., 1974). Distilled-water washing has been successful in the quantitative removal of the fraction of adsorbed phosphate in soils which is strongly dependent on the ionic strength of the contacting solution (Ryden and Syers, 1974).

The use of NaOH for the extraction of organic-bound metals was based on the fact that this fraction of the trace metal content of sludges and sludge-amended soils is expected to be associated with the functional groups of fulvic and humic acid fractions of the organic-matter complex. The standard procedure for the removal of these organic matter fractions is by extraction with NaOH (Stevenson, 1965).

Other small modifications to the Stover procedure may also improve the differentiation between carbonate- and sulfide-bound fractions of the total metal content.

Experimental

The potential of distilled-water washing in the removal of adsorbed metals was evaluated using freshly prepared Fe and Al hydrous oxide gels. The gels were prepared in the laboratory using methods described by Ryden et al. (1977) and Kinniburgh et al. (1975). Five-ml aliquots of distilled deionized water containing 0.05 g of a particular gel were added to 45-ml Oak Ridge-type polypropylene centrifuge tubes. Three ml 1 M KNO_3 were added to each tube followed by an aliquot of distilled, deionized water containing 50 to 100 µg of either Cd, Cu, Ni, Pb or Zn as the nitrate salt. Each tube was brought to 30 ml, and the suspensions were shaken for 48 hours on a reciprocating platform shaker. Following centrifugation, the supernatant solutions were decanted off and analysed for the concentration of each metal by atomic absorption spectrophotometry. The amount of each metal adsorbed by the gel used was calculated as the difference between the amount of metal added and that remaining in solution.

The hydrous oxides carrying adsorbed metal were subjected to three sequential 2-hour washings with distilled deionized water. The total solution volume during each washing was 30 ml. The hydrous oxide gel was separated from the supernatant solution by centrifugation after each 2-hour washing. The concentration of each metal in solution following each washing was determined by atomic absorption spectrophotometry. The amount of metal extracted during each washing was calculated from the solution metal concentration and the volume of water used and was corrected when applicable for metal carried over in entrapped solution from the previous extraction. A similar experiment was also conducted in which hydrous oxide carrying adsorbed metal were

subjected to the single 17-hour washing with 25 ml 0.5 M KF as proposed by Stover, et al. (1976).

The recovery of metals from reagent grade carbonates of each of the metals under investigation during 17-hour 0.5 M NaOH and 6-hour 0.05 M NaEDTA extractions was also determined. Thirty mg of each metal carbonate were weighed into 45-ml centrifuge tubes. Twenty-five ml of a particular reagent was added to each tube. After shaking for the appropriate time, residues were removed by centrifugation and the supernatant solutions were analysed for each metal.

A similar experiment was conducted using reagent grade sulfides of each metal. The extractions for the metal sulfides included those used for the metal carbonates as well as a 17-hour 2 N HNO_3 extraction and a 17-hour 4 N HNO_3 extraction at 80 C. In the case of the latter extraction, 12.5 ml 4 N HNO_3 were added to a mixture of each metal sulfide contained in a centrifuge tube. The tube was lightly capped and the suspension was heated to 80 C in a forced air oven for 17 hours. After this time 12.5 ml deionized water was added followed by centrifugation and analysis of the supernatant for each metal.

A Perkin Elmer model 103 atomic absorption spectrophotometer was used in the analysis for each metal. Standard solutions and blanks were prepared in each of the extraction solutions. The standards and blanks for the appropriate extraction solution were used for metal analysis in each extract.

Metal fractionation using pure compounds

The removal of metals adsorbed by both Fe and Al hydrous oxide gels was at least 80% and generally close to 100% complete after three washings with deionized water (Table 72). Recoveries close to 100% were observed for metals (Cd, Ni and Zn) having the least affinity for adsorption by the hydrous oxides. The lowest recoveries (approximately 80%) were observed for Cu which had the greatest affinity for both the Fe and Al gels. Recovery of Pb from the Fe gel was also low. Recovery for each metal was virtually independent of the amount of adsorbed metal present at the onset of the extraction. The data in Table 72 strongly suggest that the use of three sequential deionized water washings forms a reliable basis for the extraction of adsorbed metals from sludges and sludge-amended soils.

In contrast, the use of 0.5 M KF solution (Stover et al., 1976) was of no value in the extraction of metals adsorbed by the hydrous oxide gels. For each of the metals under investigation no metals were detected in solution following extraction with KF. In many instances there was evidence that 0.5 M KF actually promoted metal adsorption by the hydrous oxide gels.

Data for the extraction of metals from pure carbonates and sulfides

TABLE 72. WATER EXTRACTION (3x) OF METALS ADSORBED BY Fe AND Al HYDROUS OXIDE GELS.

Metal	Amt. added	Fe gel			Al gel		
		Sorbed	Extracted	% recovery	Sorbed	Extracted	% recovery
		ug /0.05 g gel			ug /0.05 g gel		
Cd	50	21.2	21.8	102	6.2	6.5	105
	100	40.0	41.2	103	16.0	16.6	104
Cu	50	50.0	41.0	82	48.8	36.1	74
	100	99.4	93.5	94	97.6	81.0	83
Ni	50	25.2	26.2	104	14.6	14.3	98
	100	37.6	38.0	101	28.0	24.4	87
Pb	50	50.0	41.4	83	44.0	45.5	103
	100	100.0	80.6	81	89.6	91.6	102
Zn	50	38.0	36.4	96	38.6	38.8	101
	100	64.6	63.1	98	73.0	69.8	96

indicated that 0.5 M NaOH should be reasonably specific to the extraction of organic-bound metals (Table 73). Only in the case of Pb and Zn were significant quantities of each metal carbonate brought into solution by 0.5 M NaOH. The partial dissolution of these carbonates during extraction with NaOH probably reflects the formation of plumbates and zincates at the high pH of this extractant solution. Despite the partial dissolution of Pb and Zn carbonates, 0.5 M NaOH extracted generally smaller amounts of metals from carbonates and sulfides than the 0.1 M sodium pyrophosphate solution used in the extraction of organic bound metals in the procedure adopted by Stover et al. (1976).

The use of a single 0.05 M NaEDTA extraction was also generally more specific to carbonate-bound metals than the double extraction with 0.1 M EDTA used in the Stover procedure. Despite the lower concentration of EDTA used in the present study, essentially 100% recovery of metals was achieved during extraction of the pure metal carbonates (Table 73). Furthermore, only small proportions of the metals were extracted from the metal sulfides using this reagent (Table 73). Only in the case of Ni and Pb sulfides were significant proportions of the metals recovered during the 0.05 M EDTA extraction.

Essentially complete recovery of metals from the corresponding metal sulfides was only achieved after extraction with 4 N HNO_3 at

TABLE 73. PERCENT RECOVERY OF METALS DURING NaOH, EDTA and HNO_3 EXTRACTION OF 0.03 g OF PURE METAL CARBONATES AND SULPHIDES.

Extractant	Metal Extracted				
	Cd	Cu	Ni	Pb	Zn
	%				
			Carbonate		
0.5 M NaOH	0	1.1	0	38.5	33.2
0.05 M EDTA	99	100	100	85.1	100
			Sulfide		
0.5 M NaOH	0	1.3	0	8.8	0
0.05 M EDTA	4.3	3.3	15	20	0
2 N HNO_3	16.3	0	46.2	44.9	94.0
4 N HNO_3,80 C	98.7	47.5	100	100	100

80 C (Table 73). An exception was observed in the case of CuS for which a recovery of only 47.5% was observed. The use of 2 N HNO_3 resulted in appreciably lower recoveries for all metal sulfides except ZnS.

Based on the data in Table 72 and 73, the procedure proposed by Stover et al. (1976) for the fractionation of metals in sludges was modified before application to the fractionation of metals in sludges, soils and soil-sludge mixtures. The fractionation scheme was as follows: exchangeable metals were extracted using 0.5 M KNO_3; adsorbed metals using three deionized water washing; organic-bound metals using 0.5 M NaOH; carbonate-bound metals using 0.05 M NaEDTA; sulfide-bound metals using hot 4 N HNO_3.

The methods adopted for exchangeable and organic-bound metals have a well-established foundation in soil analytical methods. The extraction of adsorbed metals during water washing is consistent with factors affecting metal adsorption by hydrous oxides. The data in Table 73 indicate that EDTA is selective in the dissolution of metal carbonates and extraction with hot 4 N HNO_3 results in essentially complete dissolution of metal sulfides. The generally low recoveries of total metals in the fractionation scheme proposed by Stover et al. probably

reflects the use of 1 N HNO_3 in the extraction of metal sulfides.

As indicated above, the essentially complete removal of adsorbed metals during water washing is consistent with the dependence of metal adsorption on the ionic strength of the contacting solution. The pattern of release of metals during water extraction was also consistent with the concept that metals are released as a result of a decrease in ionic strength of the contacting solution. Ionic strength is expected to approach a minimum value only after the second water washing. In most cases it was in this washing that the major release of adsorbed metal was observed.

Full experimental details of the application of the modified fractionation procedure to soils, sludges and soil-sludge mixtures are given in the following section. Preliminary application of the procedure to the fractionation of metals in a sludge-amended soil indicated that at least 90% of the total metal content was associated with the organic-, carbonate-, and sulfide-bound fractions. This preliminary application also suggested that the somewhat poorer differentiation between organic- and carbonate-bound Pb and Zn implied by the data in Table 73 may be less pronounced in the case of soils. For one soil containing 209 ug Pb/g soil, less than 5% of the total Pb was extracted by 0.5 M NaOH whereas 65% appeared in the carbonate (EDTA) fraction. A similar, although less pronounced, finding was also made for Zn.

It should be noted that the nature of metal retention by soils inevitably results in a somewhat equivocal distinction between the various metal forms based on chemical fractionation procedures. This is particularly true for the distinction between exchangeable and adsorbed forms. The high ionic strength of the KNO_3 solution used in the extraction of exchangeable metals may result in a shift to adsorbed forms. Furthermore, when amounts of organic-, carbonate- and sulfide-bound metals are high relative to exchangeable and adsorbed forms, extraction with KNO_3 and H_2O may overestimate to some extent the amounts of each metal in the latter fractions. Other less serious uncertainties arise in the distinction between organic- and carbonate-bound Pb and Zn, as NaOH may partially dissolve the carbonates of these metals. Furthermore, partial dissolution of Ni and Pb sulfides may also occur during the extraction of carbonate-bound metals using EDTA. Overall, however, the modified fractionation scheme is expected to provide a reasonably reliable indication of the distribution of trace metals in sludges and sludge-amended soils.

4.2. DISTRIBUTION OF TRACE METALS IN SLUDGE-AMENDED SOILS

Sludge-amended soils that had been incubated in excess of 50 weeks were used on this study. These samples resulted from the study outlined in Section 3. The treatment factors considered included sludges (7), soils (3) and incubation water content (2).

Fractionation of Metals

Samples of soils and sludge-amended soils (2.0 g on an oven-dry weight basis) and whole sludges (0.5 g) were weighed into preweighed 45-ml Oak Ridge-type polypropylene centrifuge tubes. Twenty-five ml 0.5 M KNO_3 were added to each tube and the suspensions were shaken for 17 hours on a reciprocal platform shaker. After this time the tubes were centrifuged and the supernatant solution was decanted and filtered through Whatman No. 40 paper before atomic-absorption analysis for each metal under investigation (Cd, Cu, Ni, Pb, and Zn). Each tube containing the soil or sludge residue was weighed to determine the volume of entrapped solution carried over into the following extraction.

The following series of sequential extractions were then performed on the residues from the KNO_3 extraction using essentially the same procedure as that described above:

3 x 2-hour extractions with 25 ml distilled deionized water;

1 x 16-hour extractions with 25 ml 0.5 M NaOH;

1 x 6-hour extractions with 25 ml 0.05 M NaEDTA;

1 x 16-hour extractions with 12.5 ml 4N HNO_3 at 80 C.

After each extraction, the solids were separated from solution by centrifugation and the supernatant solutions were decanted into storage containers for subsequent analysis. In the case of the deionized-water extraction, the supernatant solutions were also filtered prior to analysis. With the exception of the HNO_3 extraction, the volume of entrapped solution carried over from a given extraction into the following extraction was determined by weighing. In the case of the 4 N HNO_3 extraction, 12.5 ml deionized water were added to the suspensions prior to centrifugation.

The amount of each metal carried over from one extraction to the next was calculated from the metal concentrations in the prior extraction and the volume of solution from that extraction carried over into the following extraction. The amount of metal in each extract was calculated as the product of the measured metal concentration and the volume of extractant used (25 ml) plus the volume of solution carried over from the previous extraction (usually 1 to 2 ml). The actual amount of metal removed from the soil or soil-sludge mixture during a particular extraction was determined from the amount of metal present in that extract less the amount of metal carried over from the previous extraction.

In the case of sludge-amended soils, fractionation of metals was commenced only after removal of the soil solution in a saturation extract. The concentration of each metal in the saturation extract was analysed

for each system and in the case of the 1/3 bar incubation was corrected for the amount of water added to bring the soils to saturation. The amount of metals in the soil solution carried over into the KNO_3 extraction was determined from the metal concentration in the saturation extract and the moisture content of the soil after the saturation extract.

Total metal content of the soils, sludges and sludge-amended soils was determined using the 4 N HNO_3 extraction procedure like that employed as the final step of the fractionation sequence. In the determination of total metal content, however, the samples taken prior to the sequential extraction procedure were digested with acid in 100-ml digestion tubes heated to 80 C in an aluminum alloy block.

A Perkin-Elmer model 5000 atomic absorption spectrophotometer with automatic background correction was used for the determination of metal concentrations in all extracts except the KNO_3 and NaOH extracts. Metal concentrations in the latter extracts were measured using a Perkin-Elmer model 103 atomic absorption spectrophotometer. Standards and blanks were prepared in each of the extraction solutions. The standards and blanks employing the appropriate extraction solutions were used for metal analysis in each extract.

Total Metal Content of Soils and Sludges

The total metal contents of the soils used in the incubation study varied appreciably (Table 53). For all soils, amounts of Cd were less than the detection limit of 0.13 μg/g. With the exception of the Baywood soil, the amounts of Zn were larger than those for any of the other metals, ranging from 11.8 to 40.7 μg/g. Average concentration of each metal for all soils ranked in the order Zn > Ni > Cu > Pb > Cd. The concentration of each metal for each soil fell within the range of values usually observed for uncontaminated soil materials.

Total metal concentrations for the whole dried sludges indicated a wide variation with metal and sludge. As was observed in the case of the soils, the amounts of Cd and Zn usually represented the lowest and highest metal concentrations, respectively, for each sludge, with variable amounts and proportions of Cu, Ni and Pb. When the metal contents of each sludge were expressed on the basis of their incorporation into soils at the rate of 20.07 g sludge per 450 g soil used for the incubation studies, the following range of metal concentrations was observed: Cd, 0.45 to 50.4 μg/g; Cu, 23.1 to 149 μg/g; Ni, 1.68 to 86.3 μg/g; Pb, 13.4 to 272 μg/g; Zn, 68.5 to 1057 μg/g. With the exception of a few soil-sludge mixtures in the case of Ni and Zn, the amounts of each metal added to each soil as a result of the incorporation of sludge, resulted in at least a two-fold enrichment relative to the native amounts of each metal in each soil. In many cases enrichment exceeded 50 to 100 fold. Even in the case of Ni, enrichment with the metal was less than two fold in only eight out of 21 of the possible sludge-soil mixtures.

TABLE 74. METAL DISTRIBUTION IN CONTROL SOILS

	Cd	Cu	Ni	Pb	Zn
			%		
		Baywood			
Saturation	0	0	0	0	0
Exchangeable	0	0	0	0	0
Adsorbed	0	0	0	0	0
Organic	0	0	0	0	0
Carbonate	0	29	18.6	100	20.8
Sulfide	0	71.0	81.4	0	79.2
		Calhi			
Saturation	0	0	0	0	0
Exchangeable	0	0	0	0	0
Adsorbed	0	11.6	0	0	5.8
Organic	0	0	0	0	0
Carbonate	0	14.5	16.2	100	23.3
Sulfide	0	73.9	83.2	0	70.9
		Delhi			
Saturation	0	0	0	0	0
Exchangeable	0	0	0	0	1.1
Adsorbed	0	10.1	0	0	2.7
Organic	0	0	0	0	0
Carbonate	-	14.8	8.0	75.0	7.3
Sulfide	0	75.1	92.0	25.0	88.9

TABLE 75. DISTRIBUTION OF Cd IN SLUDGES AND SLUDGE-AMENDED SOILS AS AFFECTED BY INCUBATION WATER CONTENT (S = saturated, 1/3 = 1/3 bar).

Form	Rialto		LA Comp		Colton		Ontario		Escondido		LA Liquid		Kokomo	
	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3
Sludge														
Solution	n.d.*		n.d.		n.d.		n.d.		n.d.		--		n.d.	
Exchangeable	0†		0		0		0		1.1		--		1.1	
Adsorbed	0		0		0		0		0		--		0	
Organic	66.0		32.0		65.5		36.6		32.8		--		7.0	
Carbonate	26.4		50.9		34.5		51.6		53.3		--		81.0	
Sulfide	7.6		17.1		7.3		11.8		12.8		--		10.9	
Baywood														
Solution	0	0.2	0	0	0	0	0	1.8	0	1.4	0	2.2	0	0.1
Exchangeable	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Adsorbed	0	0	0	0	0	0	0	0	0	0	0	0	5.5	3.6
Organic	44.6	47.7	40.9	16.5	46.8	46.4	15.0	14.8	12.6	20.9	18.4	20.7	19.9	12.0
Carbonate	55.4	52.1	59.1	65.3	53.2	53.1	60.0	61.2	59.6	64.2	62.2	57.5	58.2	75.2
Sulfide	0	0	0	18.2	0	0	25.0	22.0	27.8	13.5	19.4	19.6	16.4	9.1
Delhi														
Solution	0	0	0	0	0	0	0	0.9	0	1.1	0	1.1	0	0.1
Exchangeable	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Adsorbed	0	0	0	0	0	0	0	0	0	0	0	0	6.4	3.9
Organic	53.3	43.3	39.6	41.8	44.6	43.8	26.5	43.1	23.3	34.5	22.3	56.9	23.2	23.7
Carbonate	46.7	56.5	60.4	58.2	55.6	56.2	60.1	51.4	54.7	59.6	60.1	42.0	60.3	70.7
Sulfide	0	0	0	0	0	0	13.4	4.6	22.0	4.8	17.6	0	10.1	1.6
Calhi														
Solution	0	0	0	0	0	0	0	0.5	0	0.3	0	1.0	0	0.2
Exchangeable	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Adsorbed	0	0	0	0	0	0	0	0	0	0	0	0	1.8	2.7
Organic	54.3	50.0	42.6	44.0	53.5	41.3	14.6	39.0	11.5	19.8	11.7	22.7	5.1	3.8
Carbonate	45.7	50.0	57.4	56.0	46.5	58.7	70.6	60.5	61.4	79.9	77.8	65.2	76.2	92.0
Sulfide	0	0	0	0	0	0	14.8	0	27.1	0	10.5	12.1	16.9	1.3

*not determined †not detected.

TABLE 76. DISTRIBUTION OF Cu IN SLUDGES AND SLUDGE-AMENDED SOILS AS AFFECTED BY INCUBATION WATER CONTENT (S = saturated, 1/3 = 1/3 bar).

Form	Rialto		LA Comp		Colton		Ontario		Escondido		LA Liquid		Kokomo	
	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3
Sludge														
Solution	n.d.*		n.d.		n.d.		n.d.		n.d.		--		n.d.	
Exchangeable	3.6		1.2		3.2		5.0		3.7		--		1.5	
Adsorbed	0.7		0.5		1.5		1.3		1.2		--		0.8	
Organic	64.4		53.8		51.9		56.2		54.0		--		57.0	
Carbonate	15.3		34.1		17.7		25.5		23.5		--		34.2	
Sulfide	16.0		10.4		25.7		12.0		17.6		--		6.5	
Baywood														
Solution	0†	0.8	0	1.4	0	1.9	0	0.5	0	0.8	0	0.3	0	0
Exchangeable	0	0	0	0	0	4.3	0	0	0	2.0	0	2.5	0	1.0
Adsorbed	0	5.7	0	4.3	0	8.8	0	6.7	1.4	3.9	7.6	2.5	4.0	3.0
Organic	58.5	70.7	57.8	66.0	63.2	69.2	61.0	67.6	39.6	70.9	56.1	70.4	50.0	54.6
Carbonate	18.2	13.8	22.7	19.3	16.2	10.4	22.5	19.7	22.1	17.0	21.8	17.6	27.1	28.2
Sulfide	23.3	9.0	19.5	9.0	20.6	5.4	16.5	5.7	36.9	5.4	14.5	6.7	18.9	13.2
Delhi														
Solution	0	0.3	0	0.1	0	0.6	0	0.5	0	0.2	0	0.3	0	0
Exchangeable	0	0	0	0	0.5	1.1	0	1.2	0	0.4	0	0.9	0	0.3
Adsorbed	6.2	2.4	5.7	3.3	4.7	3.5	3.8	3.2	2.6	2.1	7.8	4.6	6.9	4.1
Organic	56.0	72.4	54.5	57.9	56.2	70.5	49.5	64.8	47.7	67.0	50.3	60.3	47.6	51.3
Carbonate	22.1	20.6	29.7	31.5	19.9	12.4	34.9	27.1	29.4	27.3	32.4	29.9	34.7	39.7
Sulfide	15.7	4.3	10.1	7.2	18.7	11.9	11.8	3.2	20.3	3.0	9.5	4.0	10.8	4.6
Calhi														
Solution	0	0.4	0	0.1	0	1.5	0	0.5	0	0.2	0	0.3	0	0
Exchangeable	0	1.0	0	1.3	1.0	3.3	0.6	1.3	0	0	0	1.3	0	0
Adsorbed	4.4	5.7	3.6	4.8	4.6	6.6	5.5	5.5	1.9	2.5	4.7	4.7	3.5	3.3
Organic	41.9	66.7	41.4	47.2	38.2	62.3	39.9	59.4	31.1	60.6	51.1	58.9	41.3	50.3
Carbonate	26.5	21.7	39.6	40.8	20.6	14.1	34.5	28.8	29.3	32.4	31.1	30.2	36.0	43.3
Sulfide	27.4	4.5	15.4	5.8	35.6	12.2	19.6	4.5	37.7	4.3	13.1	4.6	19.2	3.1

* not determined † not detected.

TABLE 77. DISTRIBUTION OF Ni IN SLUDGES AND SLUDGE-AMENDED SOILS AS AFFECTED BY INCUBATION WATER CONTENT (S = saturated, 1/3 = 1/3 bar).

Form	Rialto		LA Comp		Colton		Ontario		Escondido		LA Liquid		Kokomo	
	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3
Sludge														
Solution	n.d.*		n.d.		n.d.		n.d.		n.d.		--		n.d.	
Exchangeable	9.3		4.7		9.0		14.4		6.8		--		0.8	
Adsorbed	0†		0		0.3		0.2		0		--		0	
Organic	42.0		33.8		54.9		34.5		36.5		--		6.8	
Carbonate	28.3		42.9		28.6		41.9		43.2		--		62.4	
Sulfide	20.4		18.6		7.2		9.0		13.5		--		30.0	
Baywood														
Solution	0	0	0	0	0	5.7	0.2	5.1	0	2.5	0	0	0	0
Exchangeable	0	0	0	0	7.3	6.5	4.0	19.9	0	12.1	0	6.9	0	0
Adsorbed	0	0	0	0	0	11.1	0	1.4	0	0	0	0	0	0
Organic	100	100	39.4	40.5	44.1	57.0	37.0	45.6	68.9	55.7	37.7	43.5	22.3	15.5
Carbonate	0	0	41.3	50.5	32.0	17.2	37.8	21.5	38.1	29.7	51.1	37.4	64.3	66.1
Sulfide	0	0	19.3	9.0	16.6	2.5	21.0	6.5	0	0	11.2	12.2	13.4	18.4
Delhi														
Solution	0	4.8	0	0.1	0	7.6	0.2	4.9	0.4	4.4	0.4	1.4	0	0.1
Exchangeable	0	0	0	0.1	7.1	11.7	0	10.5	0	7.4	0	4.8	0	0
Adsorbed	8.8	0	6.3	3.6	4.6	3.1	4.3	2.7	4.5	1.1	8.8	3.9	5.6	4.9
Organic	48.2	48.6	26.6	19.6	35.0	44.4	21.6	27.9	33.8	35.8	26.8	26.5	15.3	11.3
Carbonate	43.0	46.6	46.6	53.1	41.3	28.3	61.2	44.2	47.3	46.0	56.8	48.0	65.0	67.2
Sulfide	0	0	20.5	23.6	12.0	4.9	12.7	9.8	14.0	5.3	7.2	15.4	14.1	16.5
Calhi														
Solution	0.6	3.1	0	0.2	0.5	8.3	0.3	3.1	0.6	2.2	0.5	1.4	0	0
Exchangeable	0	0	0	0	3.3	0	2.3	4.8	0	0	4.4	7.0	0	0
Adsorbed	19.0	8.1	5.5	4.5	4.3	8.7	3.7	6.4	3.5	3.9	5.5	5.1	3.5	2.0
Organic	57.6	45.0	18.9	15.7	34.2	31.8	18.4	19.7	17.8	21.5	17.7	19.6	4.0	2.5
Carbonate	16.5	18.2	58.2	57.7	46.0	42.5	61.6	52.7	62.5	55.5	60.7	54.7	70.9	70.7
Sulfide	6.3	25.6	17.1	22.1	11.7	8.7	13.7	13.3	15.6	16.9	11.2	12.2	21.6	24.8

*not determined †not detected.

TABLE 78. DISTRIBUTION OF Pb IN SLUDGES AND SLUDGE-AMENDED SOILS AS AFFECTED BY INCUBATION WATER CONTENT (S = saturated, 1/3 = 1/3 bar).

	Rialto		LA Comp		Colton		Ontario		Escondido		LA Liquid		Kokomo	
Form	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3
Sludge														
Solution	n.d.*		n.d.		n.d.		n.d.		n.d.		—		n.d.	
Exchangeable	0†		0		0.3		0		0		—		0	
Adsorbed	0		0		0.2		0		0		—		0	
Organic	20.4		6.6		37.8		23.5		9.8		—		11.1	
Carbonate	58.6		83.3		42.8		66.5		69.4		—		82.2	
Sulfide	21.0		10.1		18.9		10.0		20.8		—		6.7	
Baywood														
Solution	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Exchangeable	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Adsorbed	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Organic	0	0	27.6	19.5	23.4	24.2	31.4	35.9	42.2	42.3	26.2	36.3	20.2	28.4
Carbonate	71.3	64.6	55.6	60.3	65.6	69.6	46.6	34.3	46.2	39.6	59.0	43.6	58.3	54.9
Sulfide	28.7	35.4	16.8	20.2	11.0	6.2	22.0	29.8	11.6	18.6	14.8	20.1	21.5	16.7
Delhi														
Solution	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Exchangeable	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Adsorbed	8.2	2.6	6.3	4.6	4.3	2.0	8.5	4.3	4.6	2.2	8.3	6.6	9.8	6.2
Organic	0	0	17.7	18.7	33.1	34.3	20.2	18.3	12.5	17.1	6.3	19.2	22.7	22.1
Carbonate	86.3	92.3	70.4	70.2	49.2	56.1	64.3	71.7	78.6	74.3	79.2	69.2	66.6	66.5
Sulfide	5.5	5.1	5.7	5.5	13.4	7.6	7.0	5.7	4.3	6.4	6.2	5.0	0.9	5.2
Calhi														
Solution	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Exchangeable	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Adsorbed	0	0	1.3	2.2	2.1	2.2	0	2.2	1.9	3.0	3.9	7.8	1.4	1.3
Organic	32.1	28.0	22.1	25.1	28.6	42.2	29.4	32.1	18.7	24.7	11.1	26.3	33.4	21.7
Carbonate	61.3	66.3	70.8	67.8	49.4	44.8	60.6	60.4	68.1	66.5	73.5	61.3	61.2	65.8
Sulfide	6.6	5.9	5.8	4.9	19.9	10.8	10.0	5.3	11.3	5.8	11.5	4.6	4.0	11.2

*not determined †not detected.

TABLE 79. DISTRIBUTION OF Zn IN SLUDGES AND SLUDGE-AMENDED SOILS AS AFFECTED BY INCUBATION WATER CONTENT (S = saturated, 1/3 = 1/3 bar).

Form	Rialto		LA Comp		Colton		Ontario		Escondido		LA Liquid		Kokomo	
	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3
Sludge														
Solution	n.d.*		n.d.		n.d.		n.d.		n.d.		--		n.d.	
Exchangeable	1.8		0.8		1.4		0.8		0.7		--		0.3	
Adsorbed	1.4		0.7		0.4		0.4		0.3		--		0.3	
Organic	60.2		39.8		67.2		66.6		56.9		--		47.5	
Carbonate	26.9		44.8		24.5		23.1		31.6		--		49.0	
Sulfide	9.7		20.9		6.5		9.1		10.7		--		2.9	
Baywood														
Solution	0†	2.4	0	0.9	0.1	3.3	0	4.8	0	3.0	0	1.9	0	0
Exchangeable	0	5.3	0	5.5	1.4	6.6	1.1	16.5	0	7.7	0.9	7.3	0.2	0.1
Adsorbed	0	0	1.0	0.9	0	3.4	1.2	1.8	1.3	1.7	4.0	2.7	2.6	2.3
Organic	47.1	48.6	41.9	38.4	50.2	58.0	51.7	45.7	52.4	54.2	60.6	45.7	49.3	43.1
Carbonate	35.7	30.7	30.4	30.8	32.6	21.9	32.6	24.2	34.4	29.1	26.5	24.3	37.5	23.3
Sulfide	17.2	13.0	26.7	23.5	15.7	6.8	13.4	7.0	11.9	4.3	8.0	18.1	10.4	31.2
Delhi														
Solution	0	2.1	0	0.1	0	3.6	0	1.3	0	1.2	0	0.4	0	0
Exchangeable	1.5	5.8	0.6	0.6	0.7	10.0	0.6	4.0	0.5	4.1	0.5	2.3	0.2	0.1
Adsorbed	2.8	2.7	4.3	3.4	4.2	2.8	4.1	3.0	3.2	2.0	7.2	5.7	5.9	4.4
Organic	48.8	47.0	42.3	41.0	43.5	51.3	49.0	53.3	48.2	50.9	51.2	51.0	51.1	54.6
Carbonate	41.8	38.9	44.7	40.5	44.3	29.2	42.3	34.5	44.0	39.7	39.9	31.8	38.3	32.0
Sulfide	5.1	3.5	8.1	14.4	7.3	3.1	4.0	3.9	4.1	2.1	1.2	8.8	4.5	8.9
Calhi														
Solution	0	0.3	0	0	0	0.9	0	0.4	0	0.3	0	0.2	0	0
Exchangeable	0	0.9	0	0	0.6	1.4	0	0.6	0	0.6	0.5	0.7	0	0.1
Adsorbed	1.5	4.3	2.3	3.8	3.7	4.6	3.3	4.7	1.8	3.1	3.3	7.3	1.0	1.2
Organic	53.1	49.5	46.0	46.2	57.3	60.8	55.6	58.0	50.9	54.8	58.2	57.3	53.5	62.1
Carbonate	37.1	33.9	43.9	46.9	32.7	28.0	36.7	32.9	37.7	39.4	34.1	31.0	33.7	34.8
Sulfide	8.2	11.3	7.8	3.1	5.7	4.3	5.4	3.4	9.6	1.8	3.9	3.5	11.8	1.8

*not determined †not detected.

Distribution of Metals in Soils, Sludges and Sludge-amended Soils

Complete results of the application of the metal fractionation procedure to soils, sludges, and sludge-amended soils are given in Tables 74-79. The distribution of each metal was expressed as a percentage of the total metal present in each sludge and soil (Table 53).

The mean recoveries in the fractionation of the total metal content of the sludge-amended Baywood, Calhi and Delhi soils (Table 76 79) was 100, 100 and 102%, respectively. The standard deviations associated with these recoveries were 7.1, 6.5 and 5.6%, respectively. Recovery of total metals was not significantly affected by the soil, sludge or incubation condition employed. Mean recoveries of between 98 and 103% were also observed when each metal was considered separately for each soil.

The mean recovery during the fractionation of total metals in the whole sludges was 107 $\pm$ 10.6% whereas that for the soils alone was 75 $\pm$ 23%. The lower and less consistent recoveries for the fractionation of native soil metals probably reflects the accumulation of errors involved in the fractionation of only small amounts of each metal.

Soils and Sludges

The native metal content of each soil existed primarily in the sulfide fraction (Table 74). An exception was observed in the case of Pb which was dominantly (100% for Baywood and Calhi soils) in the carbonate fraction. With the exception of Pb, amounts of each metal in the carbonate fraction ranged from 7.3 to 29%. In the case of Calhi and Delhi soils significant quantities of Cu and Zn were observed in the adsorbed fraction. This observation is consistent with the stronger adsorption of these metals by hydrous oxides (Table 72) and with the higher pH of the Calhi and Delhi soils which also facilitates metal adsorption (Bowden et al., 1974). The lack of organic-bound metals for each soil reflects the very low organic matter content of the soils used in the present study.

The appearance of large proportions of each native metal, except Pb, in the 4 N HNO_3 extraction is probably not indicative of the presence of native metals in the sulfide form. Native metals extracted with hot 4 N HNO_3 probably derive from structural positions in soil mineral materials. The extraction of native metals by EDTA, is probably truely indicative of the presence of these metals as carbonates, as this extractant is unlikely to remove metals from structural positions. The dominance of Pb in the carbonate form reflects the low solubility of $PbCO_3$ and suggests a dominantly anthropogenic source of this metal relative to the other metals present.

Metals in six of the seven sludges before addition to the soils were associated primarily with the organic and carbonate fractions

(Table 75-79). A sample of the LA Liquid Sludge was not available for fractionation. In four out of the six sludges examined, Cd and Ni were predominately associated with the carbonate fraction. For all sludges the major portion of the total Pb content (frequently > 60%) was present in the carbonate fraction. In contrast, Cu and Zn were primarily bound within the organic fraction. For all sludges between 52 and 64% of the total Cu was associated with organic matter. For Zn, however, in only four out of the six sludges examined was this metal primarily in the organic fraction.

The sulfide fraction for each sludge contained a variable proportion of the total metal content, but usually ranged from about 10 to 20%. In most cases the proportion of each metal present as sulfide in each sludge was less than half that occurring in either the organic or carbonate fractions.

In contrast to Cd and Pb, significant proportions of the total Cu, Ni and Zn were also observed in the exchangeable and adsorbed fractions. These proportions were usually less than 5% of the total metal content, but in the case of Ni up to 14.4% was observed in the exchangeable fraction for the Ontario sludge. The proportion of each metal in the exchangeable form was usually considerably greater than that in the adsorbed form for each sludge. This probably reflects a relatively low content of mineral material in the sludges and suggests that most of the exchange sites are associated with the organic matter in the sludge.

Sludge-amended Soils

To facilitate comparison between metal distribution in the sludges and sludge-amended soils, the metal distribution for the sludge-amended soils (Table 75-79) was calculated after correction for the amount of metal extracted from each fraction for that extracted from the corresponding fraction in the control soil. Presentation of the data in this way provides the basis for an evaluation of the redistribution of metals contained in sludges as a result of their incorporation into soil. There was no evidence that native metals in soils were redistributed as a result of incorporation and incubation of sludge and soils.

Cadmium. For sludges with a low Cd content (Rialto, LA. Composted and Colton, Table 78) which resulted in Cd contents of less than 2 μg/g for the sludge-amended soils, Cd appeared almost exclusively in the organic and carbonate forms for each soil amended with these sludges (Table 75). There was a tendency for the distribution to be weighted in favor of the carbonate form (14 out of 18 cases) despite there being a greater proportion of Cd in the organic form in two out of the three sludges.

Although a small proportion of the total Cd (7.3 to 17.1%) was present in the Rialto, LA Composted and Colton sludges in the sulfide form, only in one instance was Cd observed in this form after incubation of the sludges with the soils. In contrast the absence of Cd in

exchangeable and adsorbed fractions in the whole sludges was maintained after incubation. Only in one instance after the incubation of Rialto sludge with the Baywood soil at 1/3 bar was any substantial quantity of Cd measured in the soil solution. There were only minor variations in the distribution of Cd for these sludges as a result of the different incubation conditions employed.

For the remaining sludges with higher Cd contents, the major portion of the total Cd was with one exception found in the carbonate form after incubation with soil (Table IV.4). In the majority of the sludge amended-soils more than 60% was in the carbonate form after incubation at both 1/3 bar and saturation and in only one case did the proportion of Cd in this fraction fall below 50%. In the case of Ontario and Escondido sludges the proportion of Cd in the carbonate form increased after incubation with each soil at both moisture contents. There was also a general increase in the amount of Cd in the sulfide fraction relative to the whole sludge following incubation under saturated conditions. The increases in carbonate and sulfide bound fractions were made at the expense of organic bound Cd. Incubation at 1/3 bar resulted in appreciably lower amounts of sulfide-bound Cd relative to the amount of Cd in this form after incubation at saturation. Furthermore, for the Calhi and Delhi soils, the amounts of sulfide-bound Cd after 1/3-bar incubation were usually lower than those observed for the whole sludges.

In the case of the Kokomo sludge, which had a very high (81%) proportion of Cd in the carbonate fraction, there was a tendency for Cd to be redistributed into the organic-bound and adsorbed fractions during incubation. In fact adsorbed Cd at detectable levels was only observed in the case of incubation with the Kokomo sludge.

No detectable, exchangeable Cd was observed after incubation of any of the sludge-amended soils, reflecting the absence of this form in the whole sludges. Where sludges were applied resulting in Cd contents above 2 μg/g soil, a significant proportion (0.1 to 2.2%) of the total Cd appeared in solution after incubation at 1/3 bar.

Copper. The most pronounced and consistent trends in metal distribution in both the whole sludges and sludge-amended soils were observed in the case of Cu (Table 76). For both the whole sludges and the sludge-amended soils after incubation, Cu was predominantly associated with the organic fraction. In most instances there was a tendency for the proportion of total Cu in the organic fraction to decline relative to the sludge alone after incubation under saturated conditions. This decrease was frequently to values of approximately 40% as compared to values generally >50% for the whole sludges. The decrease in organic-bound Cu was usually associated with an increase in the amount of sulfide fraction (13 out of 18 cases). In contrast, organic-bound Cu increased (14 out of 18 cases) relative to sludges during incubation at 1/3 bar. Furthermore, the proportion of sulfide-bound Cu was in all cases appreciably lower for sludge-amended soils incubated at 1/3 bar as compared to those incubated at saturation. This decrease in sulfide-bound Cu in most cases (18 out of 21) amounted to a decrease by a factor of 4 to 6. The proportion of sulfide-bound Cu was in

most cases (17 out of 18) lower than that in the whole sludge.

The proportions of Cu in the carbonate fraction for a particular sludge-amended soil were very similar regardless of the incubation condition. In the case of Baywood soil, there were also only small differences between the proportions of carbonate-bound Cu in the whole sludge and the sludge-amended soil after incubation. The proportions of carbonate-bound Cu for the Calhi and Delhi soils, however, showed a tendency to shift to higher values relative to the whole sludge and to the corresponding sludge-amended Baywood soil.

With the exception of Kokomo sludge, incubation at 1/3 bar resulted in a significant (>0.1%) amount of Cu in the soil solution relative to systems incubated at saturation. The amounts of Cu in solution after 1/3 bar incubation ranged from 0.1 to 1.9% of the total Cu content.

With the exception of three sludge-amended soil systems, no Cu was detected in the exchangeable fraction after incubation at saturation, whereas, small but significant amounts of Cu were observed in this fraction after incubation at 1/3 bar. Regardless of incubation conditions, the proportions of exchangeable Cu in sludge-amended soils were generally less than those observed for the whole sludges. In contrast the proportions of adsorbed Cu increased in all cases during incubation at 1/3 bar, and in most cases (14 out of 18) after incubation at saturation.

Nickel. With the exception of Kokomo sludge, Ni predominantly occurred in the organic and carbonate fractions of the whole sludges, with appreciable proportions in the exchangeable fraction (Table 77). This distribution was not markedly disturbed after incubation of the sludges with each soil, and changes that were observed showed little consistency between the different sludge-amended soil systems.

The distribution of Ni in the carbonate fraction indicated a degree of dependence on the soil with which the sludge was incubated. The proportion of Ni in the carbonate fraction tended to increase in the order Baywood > Delhi > Calhi. Furthermore, the proportion of carbonate-bound Ni in the Delhi and Calhi soils was frequently greater than that for the corresponding whole sludges. The proportion of sulfide-bound Ni after saturated incubation was in some cases greater than that after incubation at 1/3 bar. This was not a consistent trend, however, as had been observed for Cu and to a large extent for Cd.

During incubation at both saturation and 1/3 bar there was a tendency for significant proportions of the total Ni to be distributed within the solution, exchangeable and adsorbed phases. This tendency was similar to that observed for Zn. The sum of the proportions of Ni in these fractions after incubation of the sludge-amended soils was frequently greater than the equivalent sum of the same fractions for the corresponding whole sludges. This was true after 1/3 bar incubation for which as much as 8.3, 19.9 and 11.1% of the total Ni was present in the solution, exchangeable and adsorbed fractions. Of all metals

investigated, Ni showed the greatest tendency to be present in the soil solution, or in the most readily displaced exchangeable and adsorbed fractions. The high proportions of total Ni in these fractions after incubation of the sludge-amended soils may reflect to some extent the relatively high proportions of exchangeable Ni in the whole sludges.

A somewhat different distribution of Ni was observed in the case of soils incubated with Kokomo sludge. The greatest proportion of the total Ni was observed in the carbonate-bound fraction after incubation, reflecting the high proportion in this fraction in the whole sludge. The amount of carbonate-bound Ni tended to increase as a result of incubation. This was particularly apparent in the case of the Calhi soil. The amount of sulfide-bound Ni declined during incubation and appeared to be redistributed to the carbonate and to some extent the organic and adsorbed fractions. In marked contrast to the incubation systems amended with other sludges, only in one instance was a significant proportion of Ni observed in the exchangeable or solution fractions.

Lead. After incubation of sludge amended soils, the distribution of Pb showed only small changes relative to the whole sludges (Table 78). Furthermore, there were only minor differences in the distribution after incubation at 1/3 bar and saturation.

As observed for the whole sludges, Pb was predominantly associated with the carbonate fraction after incubation. For Baywood soil, the proportion of carbonate-bound Pb after incubation with each sludge was in 3 out of 5 cases somewhat less than that for the whole sludges. In contrast, high proportions of carbonate-bound Pb were consistently maintained in the case of both the Calhi and Delhi soils.

For many sludge-amended soils, incubation resulted in an increase in the amount of organic-bound Pb reltive to the whole sludge (12 out of 18 cases), and the amount of sulfide-bound Pb tended to decline during incubation. The latter was particularly evident in the case of the Calhi and Delhi soils. There was no overall tendency, however, for the amount of sulfide-bound Pb to decrease after incubation at 1/3 bar.

In the case of the Calhi and Delhi soils there was a moderate shift of Pb into absorbed forms relative to the whole sludges with which the soils were incubated. A similar shift was not observed in the case of the Baywood soil. Furthermore, Pb was never detected in the exchangeable or soil solution fractions for any of the sludge-amended soils.

Zinc. After incubation of sludge-amended soils, zinc was primarily associated with the organic and carbonate fractions (Table 79). The proportion of the total Zn present in the organic fraction was usually somewhat greater than that in the carbonate-bound form. This distribution closely reflected the distribution of Zn between these fractions in the whole sludges. As was observed in the case of Pb, the proportion of Zn in each of these fractions showed little change as a result of incubation of each sludge with soil. Furthermore, there was also little effect of

incubation conditions on the distribution of Zn between the organic- and carbonate-bound forms. However, somewhat greater proportions of the total Zn were observed in the carbonate fraction in the case of the Calhi and Delhi soils, as compared to the Baywood soil.

The proportion of sulfide-bound Zn tended to increase in most cases (9 out of 12) for the Baywood soil but declined for the Calhi and Delhi soils relative to the whole sludges. There was no consistent effect of incubation conditions on the distribution of Zn within the sulfide-bound fraction. In some cases sulfide-bound Zn decreased after 1/3-bar incubation relative to saturation whereas in other cases an increase was observed.

Incubation of sludge-amended soils usually resulted in an appreciable shift of Zn into adsorbed and to some extent exchangeable forms relative to the whole sludges. This shift was particularly evident after 1/3-bar incubation, although proportions of exchangeable Zn tended to decrease slightly after incubation at saturation. With the exception of Kokamo sludge-amended soils, there was also a significant shift of Zn into the soil solution after the 1/3-bar incubation. The shift of Zn into the adsorbed fraction and the exchangeable and solution fractions at 1/3 bar, occurred from the organic and carbonate fractions in the case of the Baywood soil and from the organic and sulfide fractions in the case of the Calhi and Delhi soils. The magnitude of the shifts of Zn into the adsorbed exchangeable and solution fractions was comparable to that observed for Cu but somewhat lower than that for Ni.

Metal Concentrations in the Soil Solution

Data in Table 75-79 indicate the sludge-amended soils and incubation conditions which produce appreciable metal concentrations in the soil solution as estimated by the saturation extract procedure. Proportions of less than 0.1% of the total metal contents of each sludge-amended soil were not included in the data in Table 75-79 and the data provide no indication of the range in solution metal concentrations actually observed. The latter are presented in Table 80.

For control soils, the concentration of each metal in the soil solutions were generally below the detection limit (0.01 μg/ml) for the flame atomic absorption analysis employed. In the case of Cu and Zn, small concentrations (less than 1 μg/ml) were measured in some of the solutions extracted from the unamended control soils.

With the exception of Pb, appreciable increases in metal concentration were observed for the soil solutions extracted from the sludge-amended soils after incubation at 1/3 bar. Where comparisons can be made, the metal concentrations in solution after 1/3-bar incubation were in many cases two to three orders of magnitude greater than those observed after incubation at saturation. This trend was particularly apparent for Cu, Ni and Zn, and for Cd in the case of sludges resulting

TABLE 80. CONCENTRATIONS OF METALS (μg/ml) IN THE SOIL SOLUTION OF THE BAYWOOD, CALHI AND DELHI SOILS AFTER INCUBATION WITH SLUDGES AT SATURATION (S) and 1/3 bar (1/3).

Sludge	Cd		Cu		Ni		Pb		Zn	
	S	1/3	S	1/3	S	1/3	S	1/3	S	1/3
BAYWOOD										
Control	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.92
Rialto	<0.01	0.11	<0.01	2.55	<0.01	<0.01	<0.01	<0.01	0.12	22.1
LA Comp.	<0.01	<0.01	<0.01	0.75	<0.01	<0.01	<0.01	<0.01	<0.01	13.7
Conton	<0.01	<0.01	0.05	8.25	<0.01	16.4	<0.01	<0.01	0.34	42.0
Ontario	<0.01	1.58	<0.01	3.22	0.65	94.7	<0.01	<0.01	0.21	112
Escondido	<0.01	1.58	0.02	5.55	<0.01	3.03	<0.01	<0.01	0.10	47.8
LA Liquid	<0.01	0.62	<0.01	1.46	<0.01	<0.01	<0.01	<0.01	0.08	33.7
Kolcomo	<0.01	0.64	0.02	0.78	<0.01	<0.01	<0.01	<0.01	0.14	1.67
CALHI										
Control	<0.01	<0.01	0.02	0.15	<0.01	<0.01	<0.01	<0.01	0.07	<0.01
Rialto	<0.01	<0.01	0.02	2.39	0.02	1.44	<0.01	<0.01	0.07	5.10
LA Comp.	<0.01	<0.01	0.04	1.11	0.01	0.34	<0.01	<0.01	0.07	<0.01
Conton	<0.01	<0.01	0.04	14.6	0.27	34.8	0.05	<0.01	0.14	19.2
Ontario	<0.01	0.51	0.02	5.11	0.92	82.2	<0.01	<0.01	0.07	10.6
Escondido	<0.01	0.78	0.02	3.58	0.21	3.97	<0.01	<0.01	0.13	10.4
LA Liquid	<0.01	0.25	0.03	1.85	0.25	2.64	<0.01	<0.01	0.07	3.56
Kolcomo	<0.01	0.01	0.04	0.8	<0.01	0.23	<0.01	<0.01	0.11	3.33
DELHI										
Control	<0.01	<0.01	<0.01	0.17	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Rialto	<0.01	<0.01	<0.01	1.85	<0.01	1.50	<0.01	<0.01	0.05	33.9
LA Comp.	<0.01	<0.01	0.02	0.95	<0.01	0.25	<0.01	<0.01	0.05	1.37
Conton	<0.01	<0.01	0.03	8.55	0.07	56.0	0.05	<0.01	0.06	138
Ontario	<0.01	1.22	0.02	3.43	0.56	100	<0.01	<0.01	0.08	35.3
Escondido	<0.01	2.94	<0.01	5.12	0.08	10.0	<0.01	<0.01	0.03	43.3
LA Liquid	<0.01	0.38	<0.01	1.29	0.19	2.78	<0.01	<0.01	0.04	7.55
Kolcomo	<0.01	1.58	0.06	1.70	0.08	0.34	<0.01	<0.01	0.14	4.25

in an appreciable increase in the Cd content of the soil. For systems incubated under saturated conditions, solution metal concentrations increased by only small amounts as compared to the control soils. In many cases no increase in solution concentration relative to the control was observed. In the case of Pb, no increase in solution concentration was observed after incubation at either 1/3 bar or saturation.

The highest solution metal concentrations observed after 1/3 bar incubation were associated with Ni and Zn. Concentrations of these metals in the solution frequently exceeded 10 μg/ml. Solution concentrations of Cu were generally less than 10 μg/ml. Although for some metals the highest solution concentrations were observed for soils amended with sludges giving the highest enrichment with that metal, e.g., Ni in the case of Ontario sludge, there was no consistent pattern between solution metal concentrations and metal enrichments of the soils.

General Discussion and Summary

To facilitate discussion and comparison of the distribution of metals within the wastewater sludges and sludge-amended soils as affected by incubation conditions, the data in Table 75-79 are summarized in Table 81. In this summary the data are presented as the average distribution of each metal in each of the sludges and the sludge-amended soils for the two incubation conditions. Although some of the smaller variations in metal distribution are eliminated in this rendition of the data, the overall trends in metal distribution established in the previous section are maintained.

The averaged data for the fractionation of metals in the whole sludges resulted in the following ranking of each metal between the fractions identified in the selective extraction procedure adopted:

Cd: carbonate > organic > sulfide > exchangeable > adsorbed
Cu: organic > carbonate > sulfide > adsorbed > exchangeable
Ni: carbonate > organic > sulfide > exchangeable > adsorbed
Pb: carbonate > organic > sulfide > exchangeable and adsorbed = 0
Zn: organic > carbonate > sulfide > exchangeable > adsorbed

With the exception of the ranking observed for Cu, the ranking of the major fractions for each metal was the same as that observed by Stover et al. (1976) for sludges from twelve Indiana cities. In the study of Stover et al., Cu was predominantly associated with the sulfide fraction.

The major feature indicated by the summarized data (Table 81) is that even after incubation at either saturation or 1/3 bar, the ranking of the major fractions (organic, carbonate and sulfide) for each metal remained the same as that observed for the whole sludges. The major

TABLE 81. AVERAGE METAL DISTRIBUTION IN SLUDGES AND SOILS

	Solution	Exchangeable	Adsorbed	Organic	Carbonate	Sulfide	Solution	Exchangeable	Adsorbed	Organic	Carbonate	Sulfide
			SLUDGE									
Cd	n.a.	0.4	0	40.0	49.6	11.3						
Cu	n.a.	3.0	1.0	56.2	25.1	14.7						
Ni	n.a.	7.5	0.1	34.8	41.3	16.4						
Pb	n.a.	0	0	18.2	67.1	14.6						
Zn	n.a.	1.0	0.6	56.4	33.3	10.0						
						BAYWOOD						
			Saturated						1/3 bar			
Cd	0	0	0.8	28.3	58.2	12.7	0.8	0	0.5	25.6	61.2	11.8
Cu	0	0	1.9	55.2	21.5	21.5	0.8	1.4	5.0	67.1	18.1	7.7
Ni	0	1.6	0	41.6	44.1	13.5	1.9	6.5	1.8	43.0	37.1	8.1
Pb	0	0	0	24.4	57.5	18.1	0	0	0	26.7	52.4	21.0
Zn	0	0.5	1.4	50.5	32.8	14.8	2.3	7.0	1.8	47.7	26.3	14.8
						CALHI						
Cd	0	0	0.3	27.6	62.2	9.9	0.3	0	0.4	31.5	66.0	1.9
Cu	0	0.2	4.0	40.7	31.1	24.0	0.4	1.2	4.7	57.9	30.2	5.6
Ni	0.4	1.4	6.4	24.1	53.8	13.9	2.6	1.7	5.5	22.3	50.3	17.6
Pb	0	0	1.5	25.1	63.6	9.9	0	0	2.7	28.6	61.8	6.9
Zn	0	0.2	2.4	53.5	36.7	7.5	0.3	0.6	4.1	55.5	35.3	4.2
						DELHI						
Cd	0	0	0.9	33.3	56.8	9.0	0.5	0	0.6	41.0	56.4	1.6
Cu	0	0	5.4	51.4	29.0	13.9	0.3	0.6	3.3	63.5	26.9	5.5
Ni	0.1	3.4	6.1	29.6	51.6	11.5	3.3	4.9	2.8	30.6	47.6	10.8
Pb	0	0	7.1	16.1	70.7	6.1	0	0	4.1	18.5	71.5	5.8
Zn	0	0.8	4.5	45.9	42.2	4.9	1.2	3.8	3.4	49.9	35.2	6.4

change in ranking for the sludge amended soils was that in most cases for all metals adsorption sites became more important than exchange sites in metal binding.

The dominance of Cu in the organic-bound fraction is consistent with the high-stability of Cu-fulvic acid complexes relative to those formed with other metals (Schnitzer, 1968). The dominance of Pb and Cd in the carbonate fraction is also consistent with the low solubilities of these metal carbonates (Sillen and Martell, 1964). Ni and Zn fall within the mid- to low range of stability and solubility series for the fulvic acid complexes and metal carbonates, respectively. This is reflected by the tendency towards a more even distribution of these metals between the organic- and carbonate-bound fractions.

Although the solubility products of metal sulfides are several orders of magnitude lower than those for the corresponding metal carbonates, the formation of metal sulfides will be dependent upon the amount of $S^{=}$ available for their formation. The proportion of each metal bound within the sulfide fraction remained fairly constant relative to that for the whole sludge after incubation of sludge-amended soils at saturation. Although a maximum amount of $S^{=}$ is expected to be available for metal sulfide formation during saturated incubation, only in the case of Cu was an overall and consistent increase in the proportion of sulfide-bound metal observed. This finding possibly reflects the very low solubility product for CuS (log K = -35.2 to -37.5; Sillen and Martell, 1964).

The proportion of each metal in the sulfide fraction was usually appreciably lower after 1/3-bar incubation as compared to incubation at saturation, and in many cases was lower than that in the whole sludges themselves (Tables 75-79, 81). This finding suggested a partial oxidation and dissolution of metal sulfides under conditions facilitating an improved oxygen supply.

The proportions of carbonate-bound metals after 1/3-bar incubation also tended to be somewhat lower than those following saturated incubation (Table 81). This observation can probably be attributed to the lower pH following the 1/3-bar incubation. Following incubation at saturation, pH values for each soil were close to 8, whereas those following 1/3-bar incubation were between 4 and 7. The pH range for the Baywood soil was consistently lower than that for either the Calhi or Delhi soils. The lower pH after 1/3-bar incubation may also have contributed to the tendency for a decreased proportion of each metal in the sulfide-bound fraction.

The decrease in the proportions of carbonate and sulfide bound metals after 1/3-bar incubation relative to the corresponding metal distribution after saturated incubation, was accompanied by increases in the proportions of organic-bound metals, and particularly in the proportions of metals in the adsorbed, exchangeable and solution phases. The lower pH of the 1/3-bar incubation systems may also have been expected to decrease the proportions of organic-bound and adsorbed

metals due to increased competition between protons and metal species for organic functional groups and adsorption sites on hydrous oxide surfaces. The selectivity of these sites for metal binding depends on the relative concentrations of metals and protons in solution. The large increases in metal concentration in the soil solution following 1/3-bar incubation (Table 80) seem to out-weigh increased competition from protons in the shift of metals to the organic adsorbed and exchangeable fractions.

The greater tendency for Ni and to some extent Zn to be associated with the solution and exchangeable fractions, particularly after 1/3-bar incubation, reflects a combination of the relatively higher solubilities of the carbonates and sulfides of these metals (Sillen and Martell, 1964), the relatively lower stability constants of their complexes with fulvic acids (Schnitzer, 1968) and their moderate to low affinity for adsorption by hydrous oxides (Table 72).

Only minor differences were observed in the overall distribution of metals between the three soils used in the present study. These small differences were, however, consistent with the properties of each soil. The proportion of each metal in the carbonate fraction regardless of incubation condition was generally highest for the calcareous Calhi soil and lowest for the more acid Baywood soil (Table 81). The proportion of each metal in the adsorbed form was also generally greater for the soils with higher pH (Calhi and Delhi) than for the Baywood soil. This observation probably reflects the greater competition between protons and metal species for adsorption sites in the case of the more acid soil.

The data obtained in the present study suggest that for the soils used only a small redistribution of metals occurs when sludges were incorporated into the soils. A greater redistribution of metals may have been observed if soils with more divergent properties had been employed in the incubation studies. Of particular interest would have been soils with finer textures and higher contents of organic matter and hydrous oxides.

Despite the only minor redistribution of metals added with the sludges to each soil, the redistribution had considerable significance in relation to the potential plant-availability of the metals added. Incubation at 1/3 bar resulted in an increased proportion of the total metal content appearing in the more-readily plant-available fractions (solution, exchangeable and adsorbed) as compared to incubation at saturation. This was particularly true for Cu, Ni and Zn, although Pb showed no tendency to be associated with the exchangeable fraction or to be found in solution under either incubation condition. The extent to which metal distribution shifts upon draining a saturated, sludge-amended soil requires evaluation.

The general consistency between the metal distribution observed as a result of fractionation and the expected variation in metal distribution as affected by experimental conditions and the soils

used provides additional evidence for the reliability of the metal fractionation procedure. The distinct differences observed in the predominant distribution of some metals, e.g., Cd, Cu and Pb, and the ability to detect only small shifts in metal distribution consistent with soil type and conditions of incubation is particularly encouraging.

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